Numerical simulations on self-assembly of polyhedral particles with hundreds nanometer edge length

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NANYANG
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**NUMERICAL SIMULATIONS ON SELF-ASSEMBLY
OF POLYHEDRAL PARTICLES WITH HUNDREDS
NANOMETER EDGE LENGTH**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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OF POLYHEDRAL PARTICLES WITH HUNDREDS
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Abstract

Self-assembly of polyhedral nanoparticles has identified as one of the key approaches towards bottom-up fabrication of novel functional materials. The process of spontaneous formation of ordered structures by thermodynamics and other constraints via energy lowering pathway has been intensively studied by the research community recently. Comparing to observation of final structures or limited in-situ detection, numerical simulations are valuable tools that revealing detailed dynamics information and relationship connecting microscopic structures and physical properties. Polyhedral particles with hundreds nanometer edge length (PPHEs) are promising candidates for large scale functional material assembly. More research efforts and understanding for their assembly process mechanism are required to enable practical applications. Nevertheless, utilizing PPHE assembly could be one of the next stages for advancement in nanomaterial fabrication.

Reaching a comprehensive understanding for PPHE assembly process is intricate. This is understandable due to the complexity from both intrinsic properties and extrinsic environment for most nanoparticles systems, such as interaction description, material selection, and geometry. Among them, the large size scales of hundreds nanometer level, causes numerous problems in simulations. It is too large for molecular level simulations, yet too small to be described as bulk materials. We approached this problem by rediscovering their assembly mechanism in terms of interparticle interactions, surface modifications, and solvent-surfactant combinations.

We have performed simulations that are reasonably representative to the nature of typical PPHE particles. The properties and parameters of the building blocks can be explicitly accessed for both inner core and outer surfactants. Then we investigated the contribution from different building blocks to the interparticle interactions. We found that for PPHEs, surface-induced interaction is still in dominant role for interparticle interaction but the size and surface-bulk ratio hinders fast response in dynamics. Tuning of interparticle interaction via controlling the surfactants and environment would cause significant

changes in the thermodynamics of the assembly. Controlling parameter tests between different surface coating materials and solvents have been done for silver octahedra shaped PPHEs to plot phase diagram for assembled structure. This finding successfully relates the thermodynamic outcome of assembly with qualitative physical quantities of surfactant hydrophobicity and solvent polarity for PPHEs. Furthermore, experimental observations show good agreement with the simulation outputs, suggesting that quantitatively manipulation of the assembly outcome through changing attached surfactants and solvents could be possible. Lastly, in kinetic point of view, we utilized our previously developed methods to simulate the very initial stage of the assembly process. The whole work would serve as a preliminary attempt to exploit and connect the missing part between microscopic and macroscopic simulations.

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Abbreviations

Polyhedral particles with hundreds nanometer edge length:	PPHE
All atom:	AA
Body-centred cubic:	BCC
Carbon nanotube:	CNT
Centers of mass:	CoM
Coarse grained:	CG
Constant particle number, pressure and temperature:	NPT
Constant particle number, volume and temperature:	NVT
Face-centred cubic:	FCC
Lennard – Jones:	LJ
Molecular dynamics:	MD
Monte Carlo:	MC
N, N-dimethylformamide:	DMF
Particle Mesh Ewald:	PME
Polyvinylpyrrolidone:	PVP
Poly(ethylene glycol):	PEG
Scanning electron microscope:	SEM
Single point charge:	SPC
Space-filling polyhedron:	SFP
1-propanethiol:	C3SH
1-hexadecanethiol:	C16SH
1-Dodecanthiol:	DDT

Chapter 1

Introduction

This chapter starts a thesis devoted to developing simulation approaches for self-assembly of Polyhedral Particles with hundreds nanometer edge length (PPHE). The problems, significance, our hypothesis, and research scope will be presented in this chapter, followed by a brief introduction of the overall structure of later chapters. Results, novelty, and contributions to the field of nanoparticle assembly will also be addressed at the end of this chapter.

1.1 Hypothesis and Problem Statement

As one of the several new concepts introduced and intensively researched in the past decades, self-assembly phenomena redefines the way of viewing, processing, and understanding in microscopic world.¹⁻⁴ Nanoparticle self-assembly is scientifically important not only because it is the basis of life,⁵ but also because it holds the key relating numerous applications in nanomachine fabrications,⁶⁻⁹ quantum dots studies,¹⁰⁻¹⁷ optical plasmonics researches,¹⁸⁻²³ bio-medicine synthesis²⁴⁻²⁸, and other fields.²⁹⁻³² In addition, the bottom-up fabrication of multiple molecular architectures with controlled three-dimensional arrangements is the key to the design of novel functional materials.³³ As candidates for technological applications, nanoparticles have earned its name as promising choices. That is also why the importance of self-assembly of nanoparticles has been recognized. Moreover, such spontaneous reorganization process of building blocks into ordered structures follows mostly thermodynamic constraints, making it fascinating for the science community.³⁴

There are many simulation methods have been applied to study self-assembly. All-atomic (AA) molecular dynamics simulations are widely deployed in molecular scale assembly system, while coarse grained (CG) methods have helped in keeping push the knowledge boundary further for polymer and biological systems. Besides molecular dynamic simulations, statistical calculations such as Monte Carlo (MC) simulations are also prove useful in retrieving thermodynamic information, which can be measured in laboratory.³⁵

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Simulation study of the self-assembly process of PPHEs is crucial to successful exploitation of the mechanism. Technologically, the outcome of self-assembly on PPHEs should be able to be predicted from the chemical nature and geometries of the building blocks alone. However, due to complexity of interaction, broad selections of material, contributions from a vast list of intrinsic and environmental conditions, this would never be a simple task. Furthermore, the length scale of “nanoparticle” dramatically increases the difficulty. The situation is that the system is too large for molecular level simulations, yet too small for being treated as bulk materials. It is important to expand our

understanding of self-assembly study and cleave new technological application frontiers. Thus, a comprehensive understanding of such process is required.

Our first hypothesis aims to settle the unclearness of which mechanism dominating the interactions between PPHEs. As the basis for all later works, whether a molecular approach or a bulk approach is more appropriated needs to be determined in dealing with systems of this size regime between these two quite distinct physical pictures. Our hypothesis is that for PPHEs, even the surface atom ratio is decreased significantly, surface interaction still play a dominant role in terms of interparticle interaction.

Our second hypothesis is that by tuning of interparticle interaction via controlling surfactants and solution environment, it is possible to directly and quantitatively manipulate the outcome of the self-assembly process. This hypothesis rises from a practical reason: how could we manage to manipulate the assembly process of PPHEs. We believe the key lies in the surfactant molecules and decorated charged radicals on PPHEs before curing and annealing during the synthesis. The investigate strategy will be discussed in the following section.

Self-assembly process of these large size nanoparticles are usually considered as incompressible hard objects previously and the major effect is solely credit to their geometry nature. By rediscovering their assembly mechanism in terms of interparticle interaction, it could make it more feasible for engineering, and design of function nanoparticle products with bottom-up techniques; also these works could hopefully help in linking the missing part between molecular area and bulk area.

1.2 Objectives and Scope

To verify the first hypothesis regarding the dominant contributor of interactions for PPHEs, the investigation regarding the contribution from each component of the particle to the overall interparticle interaction would be accessed. To test such interactions, selected PPHE samples and simulation models are prepared. On one hand, the models used should be both sufficiently representative to the nature of chosen particle and

explicitly accessible for each of its component or building blocks. On the other hand, the testing particle should be typical in geometry to reflect difference between ordered SA structure and random packing in different dimensions.

To testify the second hypothesis of manipulating assembly outcomes via surfactants and environment, thermodynamic studies will be carried out. The first approach is parallel comparison between different surface coating materials under same other conditions. Meanwhile, the similar comparison could be made for solvent choice. The desired outcome should be qualitatively labeling of the contribution from surfactant and solvent into certain physical terms, and therefore making clear conclusion such as phase diagram for a given particle and/or geometry system.

Furthermore, to develop the comprehensive understanding of PPHE self-assembly, kinetic simulations based on the method developed during this work on the nucleation process would be conducted. It is not only serving as an evidence for our hypothesis, but also provides kinetic information about the initial stage of the assembly process, which is extremely difficult to be assessed except for simulation. The results have shown that initial particle density would effectively change the number of the initial nucleation clusters.

1.3 Dissertation Overview

The thesis contains the following chapters:

Chapter 1 provides the basic introduction to self-assembly of nanoparticles and the role simulation works play in this research area. The reason why PPHE assembly is underdeveloped and its significance are also illustrated. Based on these, hypotheses to tackle and explain these problems are proposed and the project scope to investigate those hypotheses is given.

Chapter 2 gives brief description on current techniques employed in self-assembly simulations. Relevant literatures reflecting different methods and their research results are reviewed. The advantages, disadvantages, and applicable conditions in dealing with PPHEs are compared. This chapter also briefly reviewed the initial stage of nucleation and some experimental observation in large sized nanoparticle self-assembly process.

Chapter 3 provides the details of simulation models of PPHEs, including its advantage and expected applicable situation. How the models are built and how this model links to the actually PPHE are discussed. This chapter also includes crucial interaction energy descriptions in the system that governing the later analysis throughout the work.

Chapter 4 illustrates the key factor played by the surface molecules in affecting the interaction between medium-sized silver core octahedron nanoparticles. Simulations to investigate the contribution from different components under various conditions are conducted. In this chapter the relationship between shell effect and the outcome of the assembly process is also deduced and discussed in thermodynamic view.

Chapter 5 studies the nucleation and growth process of PPHE. Aggregation pattern characterization criteria of octahedron particles are also discussed in this chapter. Simulations representing the dehydration procedure of colloidal system are also performed with in-situ analysis. Some key factors which having impact on nucleation and growth process are identified and discussed.

Chapter 6 concludes the thesis. The hypotheses listed in chapter 1 are proven through investigations, enabling the dynamic simulation of medium-sized shaped nanoparticles that study of the kinetics and nucleation mechanism of assembly process. These works also bring possible direction for the next stage of study.

1.4 Major Contributions of the Thesis

This research provides one of the first studies on simulation and modeling the PPHEs assembly problem. The major contributions are listed as follows: we demonstrated the

significance of surface induced factor to the interparticle interaction for polyhedral nanoparticles interaction; we developed effective modeling and characterization of interested nanoparticle system of silver octahedra covered with polymer surfactants; we related surfactant hydrophobicity and solvent dielectric constant with prediction on self-assembled 3D close packing outcome; and we preliminarily explored the initial nucleation stage of PPHE in terms of particle density from 16% to 36%.

In polymer covered silver octahedron testing system, we successfully demonstrate the quantitatively description relating the hydrophobicity of the surfactant shell and polarity of solvent with the thermodynamic outcome of the assembly process. These later experimentally observed results could serve as guidance towards rational design of bottom-up synthesized functional materials. The preliminary development in the modeling and controlling parameters of PPHE self-assembly discussed in this thesis could also pave the way for further studies in revealing kinetic information such as nucleation and growth. We expect that studies presented in this dissertation will contribute to the advancement and development in synthetic technology and industry mass-production.

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Chapter 2

Literature Review

Advancement of characterization and synthesis technology is closing up the boundary between microscopic view (molecular level) and macroscopic view (bulk level). Though the gap of the two worlds is shrinking experimentally, in simulation, most calculations still requires totally different definition, assumptions, corrections, and inputs.

A brief review of the current state of simulation technique and research related to nanoparticles system is presented here. It could be clearly noticed that each method has the unique applicable situation and corresponding achievements. That is also the reason for dynamic information on PPHEs self-assembly can also be thoughtfully accessed, with a new approximation method.

2.1 Overview of Common Simulation Techniques

As discussed and reviewed in many literatures and text books, simulation methods applied to different systems can be fundamentally different in almost all aspects. The nature of the problems, and thus the way to deal with those problems could dramatically different from each other. For instance, one system could be focusing on microscopic matters that are as small as the bonds between atoms; another system could be more interested in macroscopic way, like the collective movement of particle clusters. To begin a proper literature review, it is obligatory to assess and categorize different computational simulation methods with their designated applicable systems.

For dealing with small systems in atomic scale, it is necessary to consider chemical bonds between atoms. *Ab-initio* methods are established for the capacity of such detailed calculation physically and chemically.^{1,2} By adopting these methods that primarily based on basic quantum mechanics laws and physical constants, accurate and in-depth understanding of systems with length scale in sub-nanometer region and containing several or tens of several atoms, could be obtained.³⁻⁶

For systems that details of electron structure only play a minor role, molecular structure could be more critical principle to describe them. Molecular dynamics (MD) simulations have been used to deal with such systems for decades.^{7,8} It has been proven well suited for systems containing hundreds to tens of thousands atoms, within a frame of several nanometer regions.^{9,10} There are two major branches when dealing with problems of different focus: all atom (AA) approach and coarse grained (CG) approach. For example, investigation of single walled carbon nanotubes are commonly using all atomic models; meanwhile, geometry evolving of long chain synthetic polymer and natural protein are usually studied via CG method, which are both proven to be successes.¹¹⁻¹³

Pre-aggregated clusters, or the colloidal systems, are usually either simplified into hard objects, or when dynamic info is not vital, can be described via Monte Carlo (MC) methods.^{14,15} These systems are usually ambiguous to be dealt with because these systems are lingering between the microscopic and macroscopic world. Despite all the

ambiguity and challenge, constant development has been seen to the simulation techniques for this field. People can make progress on two directions. One direction is improving the physical accuracy. The interaction parameter used to describe inter-particle interactions can be retrieved and tuned either from experiments measurements and/or via *ab-initio* benchmark. The other direction is using valid simplification while preserving the properties of interest. Take principle study of geometry induced assembly for example, sometimes it is also a possible and efficient way that to simplify the system into solid polyhedron.^{16, 17}

2.2 Current Simulation Approaches with Large Nanoparticles System

Assembly from large nanoparticle clusters is not a new concept.¹⁸⁻²⁰ However, the principle governing this process and control techniques are still developing,²¹⁻²⁴ not to mention PPHE assembly. Many researches devoted to deal with large nanoparticles. A brief review is presented with some justification about their success and limitations.^{25, 26}

2.2.1 All-atom Molecular Dynamics Approach

In AA MD simulations, it is important to understand the molecular architecture, because molecular architecture is the key to determine physical properties of the system.²⁷⁻²⁹ For example, Lo Conte and coworkers have successfully modeled and deducted corrected parameters for the recognition sites of many types of protein molecules as shown in Figure 2.1.³⁰

Figure 2.1 Interface in 1GOT transducin $G_\alpha - G_{\beta\gamma}$. Blue and green components are backbone structure. Contacting surface between blue and green components is shaded. Red spheres are interface water molecules.³⁰ Reprinted with permission from (Lo Conte, L., C. Chothia, and J. Janin, The atomic structure of protein-protein recognition sites, *Journal of Molecular Biology*, 1999. 285(5): p. 2177-2198,). Copyright (1999) Elsevier.

Physical properties studied in AA MD simulations can further guide the design and synthesis work in industry.³¹⁻³³ Park and coworkers designed several alternated and mutated version of certain peptide showed in

Figure 2.2. Then based on the asymmetric molecular structure of the mutated peptide molecules, they predicted the possible nanoring structure could form via self-assembly of several of such peptide molecules. Furthermore, they successfully use AA MD simulations to demonstrate the validity of their hypothesis (Figure 2.3). Their work could lead to rational design of nanostructure and successful experimental synthesis.³¹

Figure 2.2 Molecular structures of T3 peptides (left) and two mutants (middle and right).³¹ Reprinted with permission from (Park, S., M. Lee, and S. Shin, A Molecular Dynamics Study on Controlling the Self-Assembly of β -Sheet Peptides with Designer Nanorings, *Chemistry-an Asian Journal*, 2015. 10(8): p. 1684-1689.). Copyright (2015) Elsevier.

Figure 2.3 Nanoring structures configurations of a) 24-mer, b) 40-mer, and c) 50-mer of a T3 peptide. The indole rings of the tryptophan residues are shown in blue. The oligoether dendrons are shown in red. Right part of the figure is the time dependence of the root-mean-square deviation from the simulations.³¹ Reprinted with permission from (Park, S., M. Lee, and S. Shin, A Molecular Dynamics Study on Controlling the Self-Assembly of β -Sheet Peptides with Designer Nanorings, *Chemistry-an Asian Journal*, 2015. 10(8): p. 1684-1689.). Copyright (2015) Elsevier.

Spontaneous assemblies of vesicles and/or wormlike structures with a randomly dispersed initial state with surfactants in solution are proven to be another great matching with AA MD simulations.³⁴⁻³⁶ One of the successful examples of AA MD could be Chaban and Prezhdov³⁷ showing that spatial confinement of water inside carbon nanotubes (CNTs) in Figure 2.4. Then substantially incensement of its boiling temperature lead the finding that a small temperature growth above the boiling point could dramatically raises the inside pressure, which could be used in drug delivery application.

Figure 2.4 AA MD simulation model includes a multiwalled CNT, composed of coaxially aligned (21,21), (26,26), and (31,31) tubes, and 1600 TIP4P water molecules inside the CNT.³⁷ Reprinted with permission from (Chaban, V.V. and O.V. Prezhdo, Water Boiling Inside Carbon Nanotubes: Toward Efficient Drug Release, *Acs Nano*, 2011. 5(7): p. 5647-5655.). Copyright (2012) American Chemical Society.

The key reason behind trustworthy results of AA and other molecular dynamics simulations is their representation of atoms and molecules in the systems.^{7, 38} Since the electronic structure and bonding process is well handled in quantum mechanics, empirical parameters are used to describe the interaction between atoms and molecules in molecular dynamics simulation. Empirical parameters used in the force fields are usually collected from experiments, previous works and rational experience fitting.³⁸ By using empirical parameters, accurate simulation results can be obtained with less time, and extend the number and size cap of simulation system from tens of atoms for typical quantum mechanics simulation to as large as tens of thousands atoms in molecular dynamics simulation.³⁸⁻⁴⁰

The idea of representing all atoms in the system is straightforward, and usually accurate.^{41, 42} However, such approach is still bonded greatly by the limitation of computational resource.^{7, 43} Even with advanced hardware such as multi-teraflop machines, when it comes to large systems like massive bio-molecules and nanoparticles colloids, the simulation would be unbearably time-consuming and even crashed down. All-atomic MD shows its limitations for large system in aspect of trying to involve the

physical mechanics information from all atoms, resulting difficulty to contain the run time in reasonable scale. So this is critical in PPHE assembly study because the number of particle of PPHE system is generally quite large.

2.2.2 Coarse Grained Approach

To overcome the previous reviewed difficulties in complexity and large number of atoms in molecular models, CG MD has been developed. It uses bead to replace relevantly stable and less important part in the structures.^{44,45} With this simplification, it has shown great success in the field of MD simulations on self-assembly processes⁴⁶⁻⁴⁸ and some are reviewed in this section.

The polymer community has adopted CG models long ago, and has achieved considerable success. Pioneer studies by Smit and coworkers⁴⁹ inspired subsequent work on surfactants and lipids.⁵⁰⁻⁵² Their work lead the study of surfactant self-assembly into the region beyond capability of AA MD, for example, cubic phase was typically beyond the computational resources limit for AA MD, but with CG beads, even phase transformation behavior could be reconstructed. With the development throughout the recent years, new features such as enhanced sampling techniques have been developed for even better and accurate description of surfactant and polymer molecules systems.⁵³

Figure 2.5 Images taken from a MD simulation of an aqueous surfactant solution.⁵⁰ Reprinted with permission from (Shinoda, W., R. Devane, and M.L. Klein, Multi-property fitting and parameterization of a coarse grained model for aqueous surfactants, *Molecular Simulation*, 2007. 33(1-2): p. 27-36.). Copyright (2007) Taylor & Francis.

As shown in

Figure 2.5, the simulation system contains approximately 800,000 CG particles and represents a solution with 80% surfactant $C_{12}E_6$ and 20% water.⁵⁰ The surfactant hydrophobic tails are shown in blue, the head groups in green and red, and the water in white. The phase transformation from initial hexagonal to final lamellar phase passes through a dislocated structure (top) before achieving the equilibrium structure (bottom).

Apart from polymer, MD simulations of biological systems also benefit from CG MD.⁵⁴⁻⁵⁸ Bio-system can easily comprise about 100 million atoms. This has far beyond the reach of AA MD region and led to the promulgation of CG models. Several CG approaches are showing substantial progress. For example, amino acid can be simplified by using BAR proteins^{59, 60} to represent the building blocks, together with groups of about 10 atoms typically coalescing into a single CG bead,⁵⁰ and then the original bulky bio molecules can be reduced to just several beads as shown in Figure 2.6.^{44, 61, 62}

Figure 2.6 CG model of outer-membrane protease T. Atoms that determining the interaction was treated with AA approach and colored in red and orange. The tail part of the molecule is colored in blue with CG tube representation.⁶¹ Reprinted with permission from (Neri, M., et al., Microseconds dynamics simulations of the outer-membrane protease T, *Biophysical Journal*, 2008. 94(1): p. 71-78.). Copyright (2008) Elsevier.

For PPHE systems, using basic building block to reconstruct the geometry shape of PPHE could be a correct approach. However, the interaction between the blocks should be taken great care to handle. In almost any CG procedure, the underlying atomistic details of the system are lost at some degree, thus it is critical to determine several key points before trusting any CG results.⁶³ One of these crucial points is the justification optimized interactions of large scale via integration and contribution from microscopic degrees of freedom. It is still noteworthy that CG MD is still under-trustworthy when it comes to explicit solution at atomic scale. Also, reduction of molecular scale information during the CG process could results in lower details and explicitness of the information retrieved.^{64, 65}

Researchers employ a varying principle to determine an interaction potential for a CG model from simulations of an AA model of the same system, in order to increase the coherence with CG model with real physical picture. It reproduces in the most optimal way the force, defined by the strict N-body potential of mean force.⁶³ However, CG potentials coming from the force matching do not reproduce accurately the pair correlation functions, and in another stream of research articles connected with CG, the authors have concentrated on the reproduction of a particular equilibrium property of the atomistic system at the CG level.^{66, 67} An empirical CG potential with fitting parameters has been commonly used to integrate out microscopic degrees of freedom that are not of direct interest. All these CG schemes are somewhat ad hoc; they have the advantage of being computationally inexpensive and are straightforward to implement,⁶³ for example, to PPHE systems.

2.2.3 Monte Carlo Approach

The MC simulation is a calculation carried out with the basic idea of using sampling and bias to iterate for the stable state of a system and this simulations technique has a long history and has been applied widely in many fields, from physics to finance.⁶⁸ MC simulations are usually treat particles as rigid non-compressible blocks in self-assembly calculations. So if we only need the final configuration that is thermodynamically stable for PPHE system, MC could offer a great deduce in computational load.

Many successful cases have been achieved in simulation shaped nanoparticles.^{69, 70} For hard spheres, Random packing and assembly have received considerable attention since they serve as a useful model for a number of physical systems, such as simple liquids,^{71, 72} glasses,⁷³ colloidal dispersions⁷⁴ and particulate composites.⁷⁵ The hard-sphere model turns out to approximate well the structure of dense-particle systems with more complicated potentials like Leonard-Jones interactions because short range repulsion between the particles is primarily responsible for determining the spatial arrangement of the particles. For some of the large random dense hard-sphere systems, a standard

Metropolis Monte Carlo algorithm was used in the very large systems to equilibrate the systems. A quantitative means of testing for local order in a system of dense hard spheres has been established. Information about volume fraction along the disordered, metastable branch of the phase diagram is revealed, from the freezing-point state to random close packing state range.⁷⁶

Apart from spheres, there are also a number of researches in dealing with polyhedra and polygons, which many PPHEs adopt these geometries. To the best of our knowledge, the first investigation of the linking probability in confined geometry was discussed by Orlandini in 1994.⁷⁷ And it still has its impact in this field throughout the time. In a recent study, Monte Carlo simulations were used to compute the linking probability of two N-edged polygons embedded on a cubic lattice.⁷⁸

Many researches also focused on an important and well-defined set of shapes, namely, regular space-filling polyhedrons (SFPs): truncated octahedron, hexagonal prism, cube, triangular prism and gyrobifastigium.⁷⁹ SFPs produced the possible assembly and possible close packing structures. And Glotzer and her co-workers⁸⁰ also made extensive expansion and compression on the relationship between the final assembly and their polyhedra shapes, via Monte Carlo runs on 145 convex polyhedral including all the Platonic, Archimedean, Catalan, and Johnson solids and some zonohedra, prisms, and antiprisms.

Figure 2.7 Summary of equilibrium structures for different SFPs. a–f, Snapshots for the various mesophases, and crystalline states for the six shapes, truncated octahedrons (a), rhombic dodecahedrons (b), hexagonal prisms (c), cubes (d), triangular prisms (e) and gyrobifastigiums (f), obtained from expansion and coexistence runs. Particle colours are used for visual effect and to detect mixing of the initial crystal layers.⁷⁹ Reprinted with permission from (Agarwal, U. and F.A.

Escobedo, Mesophase behaviour of polyhedral particles, *Nature Materials*, 2011. 10(3): p. 230-235.). Copyright (2011) Nature Publishing Group.

It was found that the particle shape can also be used to predict the general category of ordered structure that forms. Simulations at constant pressure and particle number (NPT) for truncated octahedrons and rhombic dodecahedrons indicate the presence of a plastic-crystalline mesophase for volume fractions in between the crystalline- and isotropic-phase regimes. The crystalline phases, which have a body-centred cubic (bcc) structure for truncated octahedrons and a face-centred cubic (fcc) structure for rhombic dodecahedrons shown in Figure 2.7, undergo continuous transitions to plastic-crystalline (rotator) phases, which in turn melt into isotropic phases through first-order transitions. In the rotator phases, the positional order is maintained, but the short ranged anisotropic orientation allows particles to rotate around their lattice positions.⁷⁹ They also introduced entropy maximization to understand such thermodynamic behavior of hard particles.⁸¹ Packing efficiency plays an increasingly important role toward higher density and induces a preferential alignment of flat facets.⁸²⁻⁸⁴ Because packing efficiency increases with contact area, the alignment can be interpreted as the result of an effective, many-body directional entropic force arising from the increased number of configurations available to the entire system, causing suitably faceted polyhedra to order.⁸⁵ This notion of directional entropic forces and their relation to particle faceting suggests that particle shape can be used to predict assembled structures.

Figure 2.8 Modeling and simulation of interacting lanthanide fluoride nanoplates. (a), Oleic acid tethers cause an effective attraction of nanoplate edges that is asymmetric with respect to the two edge types A and B. (b),(c) and (d) Simulation results demonstrate the formation of the alternating arrangement.⁸⁶ Reprinted with permission from (Ye, X.C., et al., Competition of shape and interaction patchiness for self-assembling nanoplates, *Nature Chemistry*, 2013. 5(6): p. 466-473.). Copyright (2013) Nature Publishing Group.

Besides 3D polyhedra, MC simulation also can deal with its 2D counterpart, polygons.⁸⁷ An empirical model for the interaction between neighboring particles for use in Monte Carlo simulations is introduced by Glotzer and coworkers.⁸⁶ In their report, as the particles do not possess significant charges or dipole moments, they interact only locally with an attractive van der Waals interaction induced by their oleic acid tethers as shown in Figure 2.8. They also assumed that the interaction energy was linearly proportional to

the contact area of the tethers, which means it was proportional to the edge-to edge contact length in the 2D model. The simulated results shows that the self-assembly of hard elongated hexagons by slowly compressing the disordered fluid. The compression was chosen to mimic the conditions present during the evaporation process responsible for nanoplate assembly in experiments. Elongated hexagons of all aspect ratios assembled exclusively into single crystals that corresponded to the parallel arrangement with few point defects and stacking faults is observed.

For polymer systems, MC simulation can also be applied to examine their assembly processes.⁸⁸⁻⁹⁰ But it is not closely related to PPHE, so only brief introduction will be made: the analytic characterization of the behavior of polymers subject to geometrical or topological constraints is a challenging task even for the simplest polymer models, such as freely-jointed chains.⁹¹

Figure 2.9 Snapshot of a Monte Carlo simulation of hard octahedra under the influence of gravity, from right to left, showing a dilute fluid, a dense fluid and a growing solid of the Minkowski type depending on the packing density and horizontal position.⁸² Reprinted with permission from (Henzie, J., et al., Self-assembly of uniform polyhedral silver nanocrystals into densest packings and exotic superlattices, *Nature Materials*, 2012. 11(2): p. 131-137.). Copyright (2012) Nature Publishing Group.

MC calculation also has employed with PPHE assembly experimental studies, trying to provide explanation that beyond the treatable region of MD simulations. Grunwald and coworkers used MC simulation in effect to understand role played by the gravity during the experiment of condensation of nanoparticles colloids.⁸² To estimate the pressures that

develop within the sediment, they carried out Monte Carlo simulations of octahedra under the influence of gravity, in an elongated box with a hard bottom wall (

Figure 2.9). To mimic the experimental set-up, simulations were started at uniform low density, enabling the particles to sediment, eventually achieving a density gradient approximately 150 μm in height. It was showing that pressures near the bottom of the model cell were sufficient for spontaneous crystallization into the Minkowski lattice.⁹² Experimental sedimentation channels feature even higher columns of dense material, and therefore pressures more than sufficient to drive crystallization. Further evidence comes from experimental waiting times.

2.3 Nucleation of Nanoparticles Assembly in Simulation

Classical nucleation theory states that nanoparticles are assembled together because of minimization of energy.⁹³⁻⁹⁵ This is something that could also be reconstructed by simulation. The formation of crystalline patterns involves the association of hundreds of thousands of molecules. It follows that the translational entropy loss associated with crystal growth is expected to be large and to increase with the size of the supramolecular adduct.^{96, 97} Figure 2.10 suggests that the molecular mass of the building blocks is a key parameter that should be optimized at the stage of chemical design. In particular, it is shown that the lighter the monomers, the larger the self-assembled architecture at equilibrium will be. Along with the shape and softness design principles, these results provide novel insight on self-assembly and will have important consequences on the design of highly robust building blocks.

Figure 2.10 Possible self-assembled materials block copolymers can form.⁹⁸ Reprinted with permission from (H Bucknall, D.G. and H.L. Anderson, *Polymers get organized*, Science, 2003. 302(5652): p. 1904-1905.) Copyright (2012) The American Association for the Advancement of Science.

Technically, to mimic the condensation, like dropping of temperature of a liquid, the most straight-forward way is to periodically reduce the velocities by a factor, or even to set the velocities to zero in simulation.⁹⁹ After such a drastic quench, time must be allowed for the system to reach equilibrium at a new temperature, as potential energy is once again converted into kinetic energy. After a liquid is quenched to a temperature well below its equilibrium freezing point, a glass can form in which particle diffusion vanishes and the system remains amorphous or a crystal can nucleate and grow.¹⁰⁰ The first observation of crystal nucleation on the computer (in a Lennard-Jones fluid) was due to Mandell et al,¹⁰¹ and since that time many systems have been studied. For example, it was shown that relatively modest changes in the potential can reproducibly alter the crystal phase formed. The moment at which nucleation can be estimated by randomizing the particle velocities

and seeing whether a crystal still forms; if it does, the barrier to nucleation has presumably been crossed.¹⁰²

2.4 Experimental Observation for Nanoparticles Assembly

Although only limited experimental reports on PPHE assembly are documented, many self-assembly experimental observations on nanoparticles with tens of nanometers length scale are reported. For example, Chan and coworkers successfully produced orderly assembled truncated nanocubes via Coulombic coupling stabilization as shown in Figure 2.11.¹⁰³

Figure 2.11 Experimentally observed superstructures of self-assembled regular (RCs) and truncated (TCs) colloidal octylaminecoated platinum nanocubes in toluene: (left) (a) square array of RCs; (b) scheme of the simple cubic structure; (c) multilayers of organized RCs; (inset) TEM

image of a RC; (right) (a) square array of TCs; (b) scheme of the fcc structure; (c) multilayers of organized TCs; (inset) TEM image of a TC.¹⁰³ Reprinted with permission from (Chan, H., et al., Colloidal Nanocube Supercrystals Stabilized by Multipolar Coulombic Coupling, *Acs Nano*, 2012. 6(5): p. 4203-4213). Copyright (2012) American Chemical Society.

One of the PPHE assembly report is by Yang and co-workers. They had observed self-assembly behavior of large nanoparticles with defined geometry through experiments.⁸² Mono-dispersed Ag polyhedral would be assembled into large ($>25\text{mm}^2$), dense supercrystals by gravitational sedimentation. N, N-dimethylformamide (DMF) was used as the assembly medium because it is an excellent solvent for PVP. In a typical experiment, a dilute solution of particles was loaded into the reservoir so that the channel filled with a uniform solution of particles. In the cases of cubes, truncated octahedra and octahedra, the structures of the dense supercrystals correspond precisely to their densest lattice packing as shown in Figure 2.12.

Figure 2.12 SEM micrographs and corresponding diagrams of densest known lattice packings of self-assembly of polyhedron lattices. d, cubes; e, truncated cubes; f, cuboctahedra; g, truncated

octahedra; h, octahedra.⁸² Reprinted with permission from (Henzie, J., et al., Self-assembly of uniform polyhedral silver nanocrystals into densest packings and exotic superlattices, *Nature Materials*, 2012. 11(2): p. 131-137.). Copyright (2012) Nature Publishing Group.

Recently, Lee reported another PPHE assembly experiment. Octahedron nanoparticles can show close Minkowski structure in various solvent conditions,¹⁰⁴ defined and calculated the theoretical densest packing factor by Minkowski in the early 1900s.⁹² As shown in Figure 2.13, in many common solvent environments, the silver octahedra spontaneously formed very ordered repeating structures. Since the substrate was flat surface, it was initially expected to be hexagonal configuration or loose packing.

Figure 2.13 SEM images of the Minkowski lattice in various solvents. The solvents are (a) water, (b) DMF, (c) 1-propanol, and (d) 1-hexanol.¹⁰⁴

2.5 Concluding remarks

In this chapter, we reviewed the common simulation methods that are widely used in nanoparticle assembly simulations. Their potential to study PPHE assembly system is also assessed. AA MD is good at accuracy, but can easily be over loaded with particle

size and number. CG MD is better at handling with larger sized and numbered particles, thanks to its coarse building blocks. The interaction between building blocks is the vital point for adopting CG MD. MC simulation is not focusing on dynamic information. So its contribution may be limited if we are aiming to simulate the actual assembly dynamic process of PPHE.

Nucleation mechanism of nanoparticles is also reviewed in this chapter. For PPHE, its size could dramatically affect many kinetic processes including nucleation.¹⁰⁵ Careful justification for PPHE system is need during modeling and applying parameters.

Furthermore, several reports on experimentally observed PPHE assembly are introduced. Some of the experimental data are later cited for comparison with simulation results.

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Chapter 3

Simulation Methodology

This chapter introduced the simulation techniques, data collection protocol and analysis criteria that are applied throughout the thesis. Firstly, how simulation models are constructed is introduced based on the fact that nano-octahedron particle possessing the size and atom number far beyond the treatable limit of all-atom molecular dynamics. Secondly, strategies of using separated modeling methods are adopted. Shrinking models with spheres as building block of octahedron is applied in multi-particle dynamics, and all-atom model is used when exploring surface interaction problem. Lastly, interaction energy for general surface case and specific stacking patterns are described. It is due to the consideration of polyhedra geometry nature of octahedron.

3.1 Modeling of Octahedral Nanoparticles

The major simulation subject is chosen to be octahedral shaped. Octahedron has several characteristics to be the desired shape used for simulation on PPHEs. Firstly it has a highly symmetric but yet polyhedra geometry. Octahedron is one of the platonic solid, making it simple to be modeled and defined by all its facets being identical equilateral triangles. At the same time, the anisotropy feature is also very strong. It has relative shape vertexes of 60 degrees, making it reasonable enough to represent the polyhedron family as well as PPHEs.

Secondly, octahedron also has well defined repeatable dense packing rules. In 3D space, it has the classic yet not simple Minkowski structure; in 2D plane, it can be closed packed into hexagonal structure; and in 1D view, they can also be aligned along their facets into a kind of AB stacking. Apart from geometry feature, octahedron is gifted from its equilateral triangle facets that usually represented by 111 growth plane. It's common in silver nanoparticles synthesis and many other materials could be maturely controlled and produced into this shape in terms of narrow size distribution, good particle perfection and various possible applied surfactants choices.

In simulation, the octahedra particles are constructed with spherical building blocks. The parameters of these spheres can be individually assigned. For instance, to mimic core shell structure, the outermost layer of spheres can either be assigned differently from the inner spheres, or attached with coarse grained surfactant molecules. The former way is more useful when dealing with large number of particles while the later method is adopted when detailed interparticle interaction is desired. The stacking pattern of the spheres is shown in Figure 3.1.

Figure 3.1 a: sample of octahedron particles modeled with sphere building blocks. b: First layer is partially peeled off. Each layer can be characterized differently.

Numbering of the spheres is done via the procedure of coordinate calculation. One primal square will be made firstly, comprising of a square assembly of spheres with desired edge length number. They are all placed at the same plane, e.g. xy plane while $z=0$. Then a next layer is constructed in the positive z axis. Each sphere will be in contact with 4 spheres from the previous layer and the edge length of this layer will naturally be 1 less than the previous layer. This procedure is done one layer by one layer, until the edge length number become 1, meaning that the tip has been constructed. Then to finish the other half of the octahedron, all spheres will get a mirror against the plane that the primal layer lies in. Prime layer gets a mirror of its own, so it will not be over counted. The most used configuration is edge length number of 10 spheres, making the total number in one octahedron to be 670.

In our shrink model, we sacrifice the time consistency by reducing the model size in exchange for the parameter accuracy. The more shrinking magnitude, the faster the model evolves compared to real case. To the maximum, the building block parameter could be close to single atom size scale. During the rescaling, we monitored the surface-bulk ratio

of the particle. To the current model in silver system, we constrain the surface-bulk ratio not exceeding 50%, corresponding to 10 spheres per edge.

Figure 3.2 Octahedron models constructed for simulations. (a) Bare Ag octahedron built using 670 Ag atoms; Ag octahedron functionalized with (b) polyvinylpyrrolidone (PVP), (c) 1-propanethiol (C3SH), and (d) 1-hexadecanethiol (C16SH).

As mentioned previously, the octahedral particles can be functionalized at the surface by attaching various surfactant molecules as shown in Figure 3.2. The attachment is done by introducing plenty of quantity of surfactants around one octahedron followed by self-adhesion and system relaxation. Different interactions between particles and solvents can be examined this way.

3.2 Coarse Grained Molecular Simulation Protocol

Like stated in section 3.1, the octahedron is not built in all-atomic scheme but with coarse grained spheres that representing a collection of atoms. And with the sphere size being shrunk, there are also several clarifications to be made before trusting any simulation results.

3.2.1 Interparticle Interaction

Since each sphere is considered as incompressible object, this section will be focused on inter-sphere interaction description, and the actual verification simulation results of interparticle interactions will be elaborated in detail in later chapters.

Within an octahedron, building-block spheres are free to move. But it is worth noting that their relative position is constrained via adding strong interaction. This is represented by the fact that the octahedron particles are not crushed or emerged; neither the surfactant gets peeled off during the assembly process. For other spheres that are treated as surface surfactant, they can be allocated with different parameters as to the core spheres. Especially, density, hydrophobicity and charge are the most commonly tuned parameters to mimic the physical properties of real surfactants.

The neighbor searching cut off of the model is set as 5 to 10 sphere diameter, depending on calculation precision, system size and time trade-off. The interaction between spheres from different octahedra will be described via traditional Lennard-Jones interaction the parameters used in the potential function are provided by GROMACS-96 force field.¹⁻⁵

3.2.2 Configuration of Initial State

The setup for initial state may directly vary the outcomes of molecular dynamics simulation. For multi-particle coarse grained MD simulation, we select the initial geometry according to the nature and purpose of the runs. The main adjustable parameters are the center-of-mass position and orientation of the octahedra. For large quantity runs that require high randomness, the octahedra are placed according to grids, which are separated by cubic with edge length from $\sqrt{2}$ to 5 times of the octahedron edge length, depending on the requirement of initial density. Then a random rotation is can be applied to each of the octahedron assigned into the grids.

For simulations on small clusters of octahedra aggregation, apart from randomized initial configuration, we also prepared patterns with ordered and semi-ordered starting geometry. Hexagonal and Minkowski structure will be most ordered packing state. The construction of these structures is straightforward by strictly following their theoretic geometry parameters about interparticle distance and Euler angle. Then from these pre-constructed hexagonal or Minkowski structure, the interparticle distance is increased to up to three times than its theoretical value, while keeping the Euler angle and diagonal axis unchanged, to produce the semi-ordered structures.

3.2.3 Particle Spatial Orientation Management

After each molecular dynamics run is finished, we retain the log and trajectory files containing energy and geometry evolution information for further analysis. The energy minimization trend will be helpful in telling the energy-favored aggregation configuration, while geometry coordinates will provide vital information for structure identification.

To precisely reveal the spatial relationship between 2 octahedra, and to determine if they are in Minkowski contact later, we need to collect their spatial coordinates and then processing pair-to-pair position relationship. This massive work was done by batch processing codes written in Python language⁶ and Matlab software.⁷

Each octahedron position and orientation was defined by six particular building spheres. These six spheres are the most central ones, forming a little octahedral shape. They are chosen as position reference by the reason that they are the least possible shifted building spheres under collision and compression between particles. The coordinates of the particle is defined as the average coordinates of the six spheres, while the spatial orientation is defined via pairing the six spheres into 3 pairs that representing the diagonal of the octahedron particle.

3.2.4 Other Notice and Limitations

From the later retrieved results, both the model and interaction settings work well to describe octahedron nanoparticles self-assembly procedures. However, this protocol also has several limitations. First and foremost is that although the dynamic information was good to be used, but the time scale is accelerated if compared with real time. And unfortunately the correlation between the simulated time scale and real world time scale has not unveiled yet. Secondly, the thickness of surfactant may not be uniform especially at sharp corners because it is coarse grained. This effect is considered not critical when the octahedra are not put too closed to each other or having violent collisions. Although uneven coverage may occur, it will be self-cured at some degree due to relocation and geometry optimization of the surfactant molecules.

3.3 Interaction Parameterization

The parameters and force fields used in the simulation are briefly discussed here. Justifications and modifications are made according to the systems of study. Interactions between different components within two adjacent particles and possible relation from interaction to the packing preference are also elaborated.

3.3.1 Force Fields and Parameters

The GROMACS 4.07⁸ simulation package and GROMOS96^{9, 10} force field were used for our MD simulations. Two neighboring atoms interact with each other through van der Waals interactions, which is treated by a 12-6 Lennard - Jones (LJ) potential summed over all pairs of atoms i and j . The LJ potential may also be written in the following form:

$$V_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad 3-1$$

where r_{ij} is the distance between the interacting pairs of atoms, σ_{ij} and ε_{ij} are the LJ parameters between atoms. It can be rewritten as below:

$$V_{LJ}(r_{ij}) = \frac{C_{ij}^{(12)}}{r_{ij}^{12}} - \frac{C_{ij}^{(6)}}{r_{ij}^6} \quad 3-2$$

where the GROMACS LJ potential parameters $C_{ij}^{(6)}$ and $C_{ij}^{(12)}$ can be computed by the GROMACS LJ potential parameters $C_i^{(6)}$ and $C_i^{(12)}$ for single atom, which can be defined as:

$$C_i^{(6)} = 4\varepsilon_i \sigma_i^6 \quad 3-3$$

$$C_i^{(12)} = 4\varepsilon_i \sigma_i^{12} \quad 3-4$$

The $C_{ij}^{(6)}$ and $C_{ij}^{(12)}$ can be computed by:

$$C_{ij}^{(6)} = (C_i^{(6)} C_j^{(6)})^{\frac{1}{2}} \quad 3-5$$

$$C_{ij}^{(12)} = (C_i^{(12)} C_j^{(12)})^{\frac{1}{2}} \quad 3-6$$

The LJ parameters $\sigma = 0.2955$ nm and $\varepsilon = 19.0790$ kJ/mol for Ag atoms were used.¹¹ Surfactant molecules include polyvinylpyrrolidone (PVP), Polyethylene glycol (PEG), 1-dodecane, hexane, 1-propanethiol (C3SH), and 1-hexadecanethiol (C16SH). Solvent molecules include DMF, 1-propanol, 1-hexanol, and toluene. These molecules used in this study were generated from the small-molecule topology generator PRODRG and their $C^{(6)}$ and $C^{(12)}$ parameters are listed from Table 3-1 to Table 3-8.

Solvent	Dielectric Constant
Water	79.7

N,N-dimethylformamide	36.7
1-propanol	20.1
1-hexanol	13.3
Toluene	2.4

Table 3-1 Physical properties of the solvents used in the self-assembly of Ag octahedra. Solvent dielectric constants are extracted from the Handbook of Organic Solvents.¹²

Atom	Mass	$C_i^{(6)}$ (kJ $\times$ mol ⁻¹ nm ⁶)	$C_i^{(12)}$ (kJ $\times$ mol ⁻¹ nm ¹²)
CH3	15.0350	0.0096138025	2.6646244e-05
CH2	14.0270	0.0074684164	3.3965584e-05
CH1	13.0190	0.00606841	9.70225e-05
O	15.9994	0.0022619536	1e-06
NR	14.0067	0.0024364096	3.389281e-06
C	12.0110	0.0023406244	4.937284e-06

Bond		
	b_0 (nm)	K_b (kJ.mol ⁻¹ nm ⁻²)
CH3- CH1	0.153	7150000.0
CH2- CH1	0.153	7150000.0
N- CH2	0.148	5730000.0
N- CH1	0.148	5730000.0
C- N	0.133	11800000.0
C- O	0.123	16600000.0
C- CH2	0.139	8660000.0

Angle		
	θ_0 (deg)	K_θ (kJ.mol ⁻¹ rad ²)
O-C-CH2	121.0	685.0
O-C-NR	120.0	560.0
CH2-C-NR	108.0	465.0
C-CH2-CH1	104.0	444.4

C-NR-CH1	125.0	375.0
NR-CH1-CH3	111.0	530.0

Table 3-2 Parameters for non-bonded and bonded interactions of PVP.

Atom	Mass	$C_i^{(6)}$ (kJ $\times$ mol $^{-1}$ nm 6)	$C_i^{(12)}$ (kJ $\times$ mol $^{-1}$ nm 12)
CH3	15.0350	0.0096138025	2.6646244e-05
CH2	14.0270	0.0074684164	3.3965584e-05

Bond		
	b_0 (nm)	K_b (kJ.mol $^{-1}$ nm $^{-2}$)
CH3- CH2	0.153	7150000.0
CH2- CH2	0.153	7150000.0

Angle		
	θ_0 (deg)	K_θ (kJ.mol $^{-1}$ rad 2)
CH2-CH2-CH2	109.5	520.0
CH2-CH2-CH3	109.5	520.0

Table 3-3 Parameters for non-bonded and bonded interactions of the C₁₂H₂₆.

Atom	Mass	$C_i^{(6)}$ (kJ $\times$ mol $^{-1}$ nm 6)	$C_i^{(12)}$ (kJ $\times$ mol $^{-1}$ nm 12)
CH3	15.0350	0.0096138025	2.6646244e-05
CH2	14.0270	0.0074684164	3.3965584e-05
OA	15.9994	0.0022619536	1.505529e-06
H	1.008	0	0

Bond		
	b_0 (nm)	K_b (kJ.mol $^{-1}$ nm $^{-2}$)
CH3- CH2	0.153	7150000.0
CH2- CH2	0.153	7150000.0

CH2- OA	0.143	8180000.0
OA- H	0.100	15700000
Angle		
	$\theta_0(\text{deg})$	$K_\theta(\text{kJ.mol}^{-1}\text{rad}^2)$
CH2-CH2-CH2	109.5	520.0
CH2-CH2-CH2	109.5	520.0
CH2-CH2-OA	109.5	520.0
CH2-OA-H	109.5	450.0

Table 3-4 Parameters for non-bonded and bonded interactions of 1-propanol and 1-hexanol.

Atom	Mass	$C_i^{(6)} (\text{kJ}\times\text{mol}^{-1}\text{nm}^6)$	$C_i^{(12)} (\text{kJ}\times\text{mol}^{-1}\text{nm}^{12})$
CH3	15.0350	0.0096138025	2.6646244e-05
CR1	12.0110	0.0055130625	1.5116544e-05
HC	1.008	8.464e-05	1.5129e-08
C	12.0110	0.0023406244	4.937284e-06
Bond			
	$b_0(\text{nm})$	$K_b(\text{kJ.mol}^{-1}\text{nm}^{-2})$	
CH3- C	0.139	8660000.0	
C- CR1	0.139	10800000.0	
HC- CR1	0.109	12300000.0	
CR1- CR1	0.139	10800000.0	
Angle			
	$\theta_0(\text{deg})$	$K_\theta(\text{kJ.mol}^{-1}\text{rad}^2)$	
CH3-C-CR1	120	560.0	
CR1-C-CR1	120	560.0	
HC-CR1-CR1	120	505.0	
CR1-CR1-CR1	120	505.0	

Table 3-5 Parameters for non-bonded and bonded interactions of toluene.

Atom	Mass	$C_i^{(6)}$ (kJ $\times$ mol $^{-1}$ nm 6)	$C_i^{(12)}$ (kJ $\times$ mol $^{-1}$ nm 12)
CH3	15.0350	0.0358	1.0792e-004
H	1.008	0	0
O	15.9994	0.0099	6.6522e-006
N	14.0067	0.0140	1.6531e-005
C	12.0110	0.0242	7.3004e-005

Bond		
	b_0 (nm)	K_b (kJ.mol $^{-1}$ nm $^{-2}$)
C- H	0.109	1.2300e+07
O-N	0.123	16600000
C- N	0.134	10500000
N- CH3	0.147	8710000.

Angle		
	θ_0 (deg)	K_θ (kJ.mol $^{-1}$ rad 2)
O-C-N	124.0	730.0
C-N-CH3	117.0	635.0
CH3-N- CH3	121.0	685.0
H-C-O	124.0	730.0

Table 3-6 Parameters for non-bonded and bonded interactions of DMF.

Atom	Mass	$C_i^{(6)}$ (kJ $\times$ mol $^{-1}$ nm 6)	$C_i^{(12)}$ (kJ $\times$ mol $^{-1}$ nm 12)
CH3	15.0350	0.0096138025	2.6646244e-05
CH2	14.0270	0.0074684164	3.3965584e-05
S	32.0600	0.0099840064	1.3075456e-05
H	1.0080	0	0

Bond		
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	$b_0(\text{nm})$	$K_b(\text{kJ}\cdot\text{mol}^{-1}\text{nm}^{-2})$
CH3- CH2	0.153	7150000.0
CH2- CH2	0.153	7150000.0
S- H	0.133	8870000.0
S- CH2	0.183	5620000.0

Angle		
	$\theta_0(\text{deg})$	$K_\theta(\text{kJ}\cdot\text{mol}^{-1}\text{rad}^2)$
H-S-CH2	96.0	405.0
S-CH2-CH2	113.0	545.0
CH2-CH2-CH2	109.5	520.0
CH2-CH2-CH3	109.5	520.0

Table 3-7 Parameters for non-bonded and bonded interactions of the C16SH and C3SH.

Atom	Mass	$C_i^{(6)} (\text{kJ}\times\text{mol}^{-1}\text{nm}^6)$	$C_i^{(12)} (\text{kJ}\times\text{mol}^{-1}\text{nm}^{12})$
CH3	15.0350	0.0096138025	2.6646244e-05
CH2	14.0270	0.0074684164	3.3965584e-05

Bond		
	$b_0(\text{nm})$	$K_b(\text{kJ}\cdot\text{mol}^{-1}\text{nm}^{-2})$
CH3- CH2	0.153	7150000.0
CH2- CH2	0.153	7150000.0

Angle		
	$\theta_0(\text{deg})$	$K_\theta(\text{kJ}\cdot\text{mol}^{-1}\text{rad}^2)$
CH2-CH2-CH2	109.5	520.0
CH2-CH2-CH3	109.5	520.0

Table 3-8 Parameters for non-bonded and bonded interactions of the hexane.

The sulfur atoms of the capping agents were attached on the Ag surface, and have negligible influence on the surface capping agent interaction. Therefore, we did not take this connecting sulfur atom into the models for PEG-SH and 1-Dodecanthiol (DDT) during the calculation of the interaction energy between the surface capping agents in various solvents. PEG parameters were taken from the CHARMM C35r force field.¹³ Water was modeled using the single point charge (SPC) model, with the bond lengths and angles held constant through the use of the SETTLE algorithm. Bond lengths of molecules were constrained using the LINCS algorithm. The cutoff distance for short-range non-bonded interactions was chosen to be 12 Å and long-range electrostatic forces were computed using the Particle Mesh Ewald (PME) method.^{14, 15}

3.3.2 Core and Shell Interactions and Surface Energy

Calculation of Ag-Ag, Ag-shell, and shell-shell interactions in PVP-coated Ag octahedra-slab is described as following. The total interaction energy (E_{int}) of the system in water is derived using:

$$E_{\text{int}} = E_{\text{Ag-Ag}} + 2 \times E_{\text{Ag-shell}} + E_{\text{shell-shell}}^{\text{solv}} \quad 3-7$$

The Ag-Ag, Ag-shell, and shell-shell interactions are calculated using the following equations:

$$E_{\text{Ag-Ag}} = E_{\text{Ag1}} + E_{\text{Ag2}} - E_{\text{Ag1+A}} \quad 3-8$$

$$E_{\text{shell-shell}}^{\text{solv}} = E_{\text{shell1+shell}}^{\text{solv}} - (E_{\text{shell1}}^{\text{solv}} + E_{\text{shell2}}^{\text{solv}}) \quad 3-9$$

$$E_{\text{Ag-shell}} = \frac{[(E_{\text{Ag1}} + E_{\text{shell2}} - E_{\text{Ag1+shell}}) + (E_{\text{Ag2}} + E_{\text{shell1}} - E_{\text{Ag2+shell1}})]}{2} \quad 3-10$$

where the energy terms E_{Ag1} , E_{Ag2} , E_{shell1} , and E_{shell2} are the individual potential energy of the Ag cores (Ag octahedra or Ag slabs) and the shell polymer chains on the Ag cores. The term $E_{\text{Ag1+Ag2}}$ refers to the interaction energy of the two Ag cores, while the term $E_{\text{shell-shell}}^{\text{solv}}$ refers to the intermolecular interaction energy between the two shell polymer chains in various solvents, the $E_{\text{shell1+shell2}}^{\text{solv}}$ term refers to the total shell-shell potential energy of the system, and the $E_{\text{shell1}}^{\text{solv}}$, $E_{\text{shell2}}^{\text{solv}}$ terms refer to the individual intramolecular interactions of the respective shell polymer chains in various solvents. The energy terms $E_{\text{Ag1+shell2}}$ and $E_{\text{Ag2+shell1}}$ refer to the total potential energy between the Ag core and shell polymer chains on the neighboring Ag core. The numerical suffixes for Ag and shell refer to the arbitrary labeling of the Ag cores and shell polymer chain in the dimer.

After formulating the interaction within one pair of octahedron particles, the overall interparticle interaction effect on the 3D and 2D assembly is derived as follows. During the self-assembly process, our hypothesis suggests that the energy between octahedron particles (p-p), between octahedron particle and solvent molecules (p-s) and between solvent molecules (s-s) will determine the type of assembly formed. The Minkowski lattice maximizes the overall Ag octahedra surface areas in contact. For example, we compared the tendency of forming Minkowski structure and commonly known hexagonal structure. For one octahedron assembled into bulk Minkowski structure, the energy difference before and after such process is:

$$\Delta E_{\text{Minkowski}} = \frac{8S}{3} \cdot E_{\text{p-s}} + \frac{8S}{3} \cdot E_{\text{p-p}} + V_{\text{Minko_ex}} \cdot E_{\text{s-s}} \quad 3-11$$

where S is the area of the triangular [111] facet of the octahedra and $V_{\text{Minko_ex}}$ refers to the exclusion volume of the solvent after Minkowski assembly is done.

On the other hand, the energy difference for the next densest packed hexagonal close-packed structure is:

$$\Delta E_{\text{Hexagonal}} = 3S \cdot E_{p-s} + \frac{5S}{2} \cdot E_{p-p} + V_{\text{Hex,ex}} \cdot E_{s-s} \quad 3-12$$

where $V_{\text{Hex,ex}}$ corresponds to the exclusion volume of the solvent after hexagonal assembly. For the formation of Minkowski lattice to be favored, the $\Delta E_{\text{Minkowski}} < \Delta E_{\text{Hexagonal}}$ relationship should be satisfied, meaning:

$$E_{p-p} + \frac{6(V_{\text{Minko,ex}} - V_{\text{Hex,ex}})}{S} E_{s-s} - 2E_{p-s} < 0 \quad 3-13$$

3.4 Concluding remarks

In this chapter we elaborated the simulation techniques used in the simulations. Simulation models are constructed to be rational both in physics representation and ability to be accessed and modified. Different interactions originated from different part of the system under different environment are believed to hold the key in answering the self-assembly process of PPHEs. As a typical example of PPHE, octahedral particles with decorated surfactants will be used in simulation under various conditions in the following chapters. CG modeled octahedron core with AA modeled surfactants models will be adopted when the focus is in interaction between two adjacent particles, CG model octahedron core and also CG modeled surfactants models will be applied when dynamic simulation are performed on system with large amount of particles.

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Chapter 4

Study of Interparticle Interactions and Prediction in Self-Assembly

This chapter illustrates the key governing factor to the interaction between medium-sized silver core octahedron nanoparticles. Thorough simulations regarding of the interaction contributed from different components of the octahedron nanoparticles have been conducted under various conditions. It is discovered that the shell part of the octahedron nanoparticles plays a critical role. Via surfactant modification, such tunable component can inspire great applications. Simulations on shell effect of different surfactants and solvents also suggest a high impact on the characteristic self-assembled structures of the systems. With further exploration on the combination of surfactants and solvent choice, thermodynamic prediction of the assembly outcomes deduced from these combinations would be possible. Furthermore these verifications and calculations would be later lead to the vast molecular dynamic simulations on massive octahedron nanoparticles systems with in-situ analysis for the nucleation and growth procedures in chapter 5.

4.1 Interaction Contributions of PPHEs

As bridges linking between bulk materials and molecular level structures, PPHEs are drawing great scientific interests. Bulk material is regarded of constant physical properties independent of its size, while nanoparticles behave on the opposite way. With their size shrinking towards the nanoscale, the surface effect of the material becomes significant, which is understood by the increment of the percentage of surface atoms. Another key point for PPHEs is that they can easily adopt the core-shell structure, which can have completely different surface effect to the naked core. Much research has been devoted to this core-shell relationship investigation.

For octahedron silver nanoparticles, the additional polymer shell may also play a critical role in terms of interparticle interactions. For that reason, both the simulation models and experimental subjects should take consideration of this shell contribution. Based on results later discussed in this chapter, it was shown that the shell-shell and shell-solvent interaction overwhelm the contribution from beneath silver core. Therefore, we arrived at the hypothesis introduced in the beginning of this thesis: By controlling the combination matchup of the polymer that covering silver octahedron nanoparticles and the solvent environment of the system, self-assembly result of the system is thermodynamically predictable.

This hypothesis would firstly be verified via interaction investigation between different components of the nanoparticles. After we have supporting evidence that showing shell-induced interaction is in dominant state, a series combination of shell and solution candidates of different affinity to each other would be introduced. Subsequently, based on their interaction and potential energy calculations, predictions of their assembly outcomes would be drawn and then verified via experiments.

The interaction energy calculation protocol would be as following throughout this chapter: For simulation involving background slabs, we put 8 PVP molecules of repeating unit of 125 on a silver slab of $8.85 \text{ nm} \times 8.96 \text{ nm} \times 4.50 \text{ nm}$ size. For simulation involving surfactants over octahedron nanoparticles, we let 8 PVP molecules of 125 repeating units

to freely being absorbed on a silver octahedron of edge length of 4.4 nanometers. After relaxation, this particle is duplicated for interparticle interaction calculation. For simulations between surfactant molecules, all-atomic models are applied. The size of the molecules are selected to be of 125 repeating units for PVP and kept to similar molar mass for other surfactants molecules. The molecules are firstly allowed to reach equilibrium separately in corresponding solvent environment before brought together. After they are put together, the rough damping period is omitted in the figures due to less importance. The energy interaction calculations are carried out by the following: at any time step of interest, we subtract the total energy of the system with the energy at equilibrium state for each of the interacting component of the system.

4.2 Investigation of Shell-induced Interaction

The simulations to investigate interaction contributed from different components of the nanoparticles were divided into two sections. Firstly, the generalized simple slab model would be used. After showing supportive results that polymer shell-shell effect is much larger than that of the rest of contributions, the shrunk octahedron model would be applied. For the sake of typicality and simplification, all models are unified with PVP shell covering silver octahedron core (silver slab for 2D cases) in water solution environment.

4.2.1 Individual Component Contribution for Interaction between 2D Slabs

Figure 4.1 Silver slabs decorated with polymers and solution molecules. Inter layer distance x is tunable for interaction profile calculation.

The first step of investigate the interaction contribution is to acquire an extent information on local interactions of Ag octahedron particles on surface. Ag slabs of dimension of $8.85 \text{ nm} \times 8.96 \text{ nm} \times 4.50 \text{ nm}$ are created to reproduce this short range surface-induced interaction. On one side of the slabs we added 8 PVP chains, with each chain was built of 125 repeat units. The two PVP-decorated Ag slabs were placed with PVP side facing each other in a simulation box of $8.85 \text{ nm} \times 8.96 \text{ nm} \times 24 \text{ nm}$. This box is filled in with water molecules to represent the aqueous solution environment. The cutoff distance for non-bonded interactions was set to be $12 \text{ \AA}$. A set of inter-slab distance was introduced and fixed. Several sample illustration was shown in Figure 4.1. All silver atoms positions were fixed, while PVP chains are allowed to relax. Periodical boundary conditions were applied to prevent PVP molecules escaping from the testing region. This is important especially when inter-slab distance decreased, the PVP molecules had more tendency to be pushed out.

The relaxation procedure was done for 1 ns of dynamic run. After that, the equilibrium system of these two PVP-decorated Ag slabs was placed into an $8.85 \text{ nm} \times 8.96 \text{ nm} \times 60 \text{ nm}$ box for interaction pair potential energy extraction. The cutoff distance for a short-

range non-bonded interaction at this stage was set at 40 Å to balance the number of atoms included in searching range and the requirement that cut-off distance cannot be larger than half of the dimension of the box. The results are shown in Figure 4.2.

Figure 4.2 Interaction energy profile of PVP decorated silver slabs. The inset shows the convergence of the energy changes at longer surface separation distances; black line represents the total interaction energy. (a) total energy, (b) Ag-Ag, Ag-PVP, and PVP-PVP separated plot.

From the results, the first impression is that the plot of PVP-PVP interaction almost matches perfectly with the total interaction plot. The PVP-PVP interaction makes most part of both repulsive component in very near range and attractive component beyond the equilibrium point. This PVP-PVP interaction has a quite deep potential well of approximately $-4670 \text{ k}_B\text{T}$ at an inter-slab distance of 3.8 nm . Compared to the PVP-PVP interaction, the PVP-Ag and Ag-Ag interactions are much less significant. They are constantly remaining near zero unless the slabs are very close to each other with distance less than 3 nm . When it's near either the equilibrium distance of 3.8 or the region that the overall interaction is approaching to zero, their contribution is still less than $0.1 \text{ k}_B\text{T}$. Even for around distance of 3 nm , the adsorption energy of PVP-PVP is still about 17 times greater than the adsorption energy of Ag-PVP. However, it is usually reported as high for metal-metal attraction interaction. To further confirming of the insignificance of contribution from non-PVP interaction, we prepared a separate model to test Ag-Ag interactions in the absence of PVP decoration.

Figure 4.3 Modeling of the short-ranged Ag-Ag interactions in the absence of PVP chains using two Ag slabs in water. (a) Changes in Ag-Ag interaction energy of the system as a function of surface separation distance. (b) Schematic illustration of the pure Ag slabs.

Figure 4.3 presents an identical simulations set-up but without PVP molecules. From the results, we can confirm that Ag-Ag interactions are indeed shorter-ranged. Attractive interactions between the naked Ag slabs only take effect for distance less than 3 nm. At distance of 3 nm, though the interaction is stronger than the case with PVP decoration, but the number is still limited to 10 $k_B T$. This difference in Ag-Ag interaction energy with and without the presence of PVP shell indicates that the Ag-Ag interaction energy is effectively shielded by the surface capping agents. The thickness requirement any not be too large since the thickness of PVP in simulation is no large than 2 nm.

Thus we could assume that the overall interaction energy is dominated by the attractive and repulsive interactions from the PVP-PVP pair, while the Ag-Ag and Ag-PVP interactions are considered weak and short-ranged. This test allows us to bridge the small-sized models in the simulations with the large actual particles in reality, enabling later comparison work.

4.2.2 Shell-induced Interaction between 3D Octahedron Particles

After confirmed assumption of interaction in 2D cases, we proceed to 3D octahedron model to mimic dimer system interaction. The dimer system can be interoperated as the simplest type of self-assembled cluster during self-assembly process. Figure 4.4 shows the results from the interaction energy change of a system containing two PVP-covered silver octahedra surrounded by water molecules. The interaction energy was recorded at different inter particle distance. Similar to the 2D runs, the total interaction energy of the dimer system (E_{int}) consists contribution from three components: interaction between the two silver octahedron cores (E_{Ag-Ag}), interaction between one silver octahedron core and the PVP shell of the other octahedron particle (E_{Ag-PVP}), and interaction between the two PVP shells ($E_{PVP-PVP}^{solv}$), respectively. E_{int} is expressed as following:

$$E_{int} = E_{Ag-Ag} + 2 \times E_{Ag-PV} + E_{PVP-PVP}^{solv} \quad 4-1$$

The distance between octahedra is defined as the facet-to facet shortest distance between two particles. The distance is only changeable along the line connecting the two centers of mass of the each octahedron, showing in inset of Figure 4.4a. This prior conception of conducting this set of simulation is to explain in 3D octahedron assemblies, which are the dominating interactions to be taken credit for. Previously most works applied pre-allocating assumptions of pure attractive (between Ag cores) or repulsive forces (between surface-bound polymer chains) to certain components. In addition, the solution environment of all simulations is also set as aqueous solution, enabling direct comparing for experiments done in similar set-ups.

Originally, the edge length of the octahedron core is about 44 Å. 8 PVP chains, each having 125 repeat units, were randomly introduced near the octahedron. After dynamic relaxation run, they are all adsorbed onto the Ag octahedra surfaces. With this additional PVP polymer shell covering the octahedron, the edge length increases to approximately 6nm to 8 nm, depending on the polymer chain local configuration. This dimer system adopts the geometry of type 3 contact discussed in chapter 3. The simulation box has geometry of 24nm × 12nm × 12nm. The cutoff distance of short-range non-bonded interactions was set to be 12 Å. A series of different inter-particle distance were applied to this model. During the simulation, it is fixed for the silver atoms, while PVP molecules are free to relax in the process. The reason for choose the nearest distance of 4.9 nm is because that if the octahedron particles are getting to close for the initial configuration, before the repulsive force to separate them, the PVP chains could likely be squeezed to either escape from the interested region or just diffuse to adjacent facets. To avoid these artificial confusions, the initial inter-particle between nearest facet was recommended to be larger than 5 nm. The simulation ran for 1 ns to achieve a relative stable state. After that, it would be transferred to a simulation box of 80nm × 40nm × 40nm for interaction scanning. The cutoff distance for short-range non-bonded interactions at this stage was set at 40 Å, aiming to pick up most of the atoms accountable in the list of searching.

Figure 4.4 Interaction profile of a PVP-functionalized Ag octahedra dimer in water. a, total interaction energy of the dimer system as a function of surface separation, denoted as x in the schematic shown in the inset; b, the separation plot of interaction energy contributed from Ag-Ag,

Ag-PVP, and PVP-PVP interactions. Inset shows the energy changes converging at larger surface separation distances; black line represents the total interaction energy; c, simulation snapshots illustrating the increasing extent of PVP chain association as the surface separation decreases from $x = 5.5$ nm to 4.7 nm. At 4.7 nm, the attractive PVP-PVP interactions become repulsive due to the chain association.

The extracted interaction energy information is shown in Figure 4.4. The overall interaction profile takes a potential well shape. As expected, contributions from PVP-PVP interactions are in dominant ratio Figure 4.4b. At near distance around 4.7 nm, the interaction energy would go through its local minimal point. This means its first derivative, or the interaction force will change its sign, switching between attractive and repulsive. Such repulsive interaction at distance less than 4.7 nm is believed contributed from the repulsive part of van der Waals interaction associated between PVP chains and neighboring Ag cores Figure 4.4c. The interaction energy has a minimal point at around 4.9nm. The attraction originated from PVP-PVP interaction reaches its maximum value of approximately $-91 \text{ k}_B\text{T}$ at this distance and contributing to almost 97 % of the overall interaction. After the particles are placed further apart, the interaction energy goes to positive and close to zero, meaning it could be beyond the range of surface interaction but at the hands of thermal fluctuations Figure 4.4a. Such strong matching between the overall interaction and that contributed from PVP chains confirmed its dominant influence in the system, suggesting that PVP-based attraction could be the driving force to bring the dimer close to each other during the assembly.

Figure 4.5 Interaction profile on octahedra covered with thinner PVP shell of 50 repeating unit. a, potential energy plot with enlargement near 1 nm separation. b, illustration on contacting orientation. It is identical to the orientation in Figure 4.4.

It's also suspected that the equilibrium separation distance between the dimer is highly affected by the PVP shell thickness. A set of simulation with PVP shell of less thickness was performed as shown in Figure 4.5. The repeating unit number of PVP chain for this set is 50. It could be found that the equilibrium interparticle distance is reduced to around

1nm. Compared to 4.7nm in 125 repeating unit runs, the interaction contributed from PVP-PVP shell still overwhelms the interaction involving silver cores. Furthermore, the difference in average thickness between 50 repeating unit PVP shell and 125 repeating unit is approximately 1.8nm. When doubled for dimer, this difference compensates a considerable amount of interparticle distance change. This effect could be possibly understood via the surface coverage of PVP shell. For shorter PVP shells, there are more shell molecules having enough space to lie down on the particle surface, while for longer chain cases, they would be forced to “stand up” to contribute more vertical thickness when there are not enough free space on the particle surface.

Figure 4.6 Interaction profile on octahedra covered with thinner PVP shell of 50 repeating unit. a, potential energy plot with enlargement near 6 nm separation. b, illustration on edge-edge direction contacting orientation.

The octahedron particles are anisotropic. This means we need to also consider the geometry effect on the interaction profile. Face to face contact (we name it Type 3 contact in chapter 5) was used in previous simulation, and we also performed edge-to-edge contact simulations (Figure 4.6). The simulation set-up is similar to that of Figure 4.4

expect the dimmers are not in type 3 geometry but aligned “shoulder to shoulder”, with their nearest edges parallel to each other. Apart from the equilibrium interparticle distance locating at around 4.3 nm, the results still indicate a negligible contribution from the core related interaction. The equilibrium distance is smaller than that of type 3 configuration by approximately 0.6 nm. One possible explanation could be that at edge region, the average thickness of PVP chains is smaller than other part of the particle, resulting a shorter stable distance between the shell molecules.

In conclusion, these 3D octahedron simulations show the dominant position of attractive interaction between PVP shells. Also, this interaction is distinct from depletion-induced attraction as there are no free polymer molecules included in the simulation boxes. It is noteworthy to clarify that all polymer covered shaped particles are subjected to the consideration of geometry roundness. If the amount and thickness of the polymer shell is too large, the particle may practically become a sphere. Lastly, since the simulation is focused on the interaction between nanoparticles and their major component’s effect on the self-assembly process, the results are all considering the presence of solution. Thus direct comparison the interparticle distance between the simulation and experiment would be meaningless as drying effect and other kinetics may kick in. For the comparison with experiments discussed in the next session, we refrain from over-detail comparison but only focusing at the assembled geometry patterns.

On the other hand, there are some facts to be noted due to the adaption of shrink model CG method here. Firstly and foremost, the shrinking model decreased the particle size up to 100 times than the synthesized nanoparticle. The dramatic reduce in size and hence mass of the particles, would greatly increase the mobility of the particles, giving rise to total inconsistency of simulated timescale to real time. Secondly, the surface-bulk ratio of the particles is reversely linear to the edge length ($\frac{3\sqrt{6}}{a}$, where a is the edge length and unit is $length^{-1}$), the surface ratio would be increased up to tens of several times than the real case. The effect of these deviations from reality would be justified in two ways: first, the time consistency is not our priority due to the fact that interparticle interaction could be considered as time-independent. Secondly, from the results in section 4.2.1, we

already found the dominance of surfactant-induced interaction in our system, so that the linearly increased surface-bulk ratio would be a minor error source at its most.

4.3 Thermodynamic Prediction of Assembly via Surface Interaction

Having recognized the governing role of attractive PVP shell-shell interactions in octahedron nanoparticles interactions, we then investigate how solvents-surfactant combination impacts the molecular interactions, furthermore the nanoparticles self-assembly process. To answer the question of how the changes of capping polymer layer (PVP, PEG-SH, C12H25SH) in various solvents (water, DMF, 1-propanol, 1-hexanol, and toluene) would affect the interaction energy, which would later lead to different structural as the self-assembly results, we performed a series of MD simulations. For the focus on the shell molecule interaction, we applied all-atomic molecular dynamics simulation models rather than coarse-grained models. This also allows the increase of accuracy on the interaction profiles for polymer molecules in solution environment.

4.3.1 Interaction Energy Definition for Polymer Shell Molecules

The following simulations all serve to connect the capping shell of silver octahedron nanoparticles to their role in the self-assembled structures. By quantifying the solvent-dependent molecular interactions between polymer chains, we aim to correlate these interactions to the different packing patterns, which can be observed by experiments. The molecular interactions are monitored by sampling all the interaction energy between two polymer chains in various solvents environment at thermodynamic equilibrium. The interaction energy between two polymer chains in various solvents ($E_{\text{polymer-pol}}^{\text{solv}}$) is defined as:

$$E_{\text{polymer-polymer}}^{\text{solv}} = E_{\text{polymer1+polymer2}}^{\text{solv}} - (E_{\text{polymer1}}^{\text{solv}} + E_{\text{polymer2}}^{\text{solv}}) \quad 4-2$$

The numerical suffixes correspond to the arbitrary naming of the two polymer chains. $E_{\text{polymer-polymer}}^{\text{solv}}$ is calculated by subtracting the individual intramolecular interactions of the respective polymer chains in the various solvents ($E_{\text{polymer1}}^{\text{solv}}$, $E_{\text{polymer2}}^{\text{solv}}$) from the overall polymer potential energy of the system ($E_{\text{polymer1+polymer}}^{\text{solv}}$).

The polymer clusters used in the simulation were built by all-atomic models according to the followings species: 2 PVP chains, each built with 125 repeat units, 2 clusters of 14 PEG chains, each built with 23 repeat units, and 2 clusters of 83 dodecane chains, with total atom number around 2000. The two clusters (the distance between them within 1 nm) were put into the simulation box, followed by introducing the various solvents.

Simulations were performed using the NVT ensemble, the temperature was maintained at 300 K using the Berendsen temperature coupling method. Simulations were run over 8 to 60 ns in steps of 2 fs, over the course of which the potential energies of the ligands interacting with the solvents became stable. In addition, snapshot pictures were prepared using VMD. The equilibrium trajectory was then used for analysis. The interaction energy profiles of the three components ($E_{\text{PVP1+PVP2}}$, E_{PVP1} , and E_{PVP2}) were derived at the stage that the dimensions of the simulation box conserved.

4.3.2 Simulation Prediction and Experimental Comparison

To steer towards a more universal understanding of solvent-surface capping agent interactions and their impact on the Minkowski lattice formation, we conduct further self-assembly experiments and simulations using additional hydrophilic and hydrophobic ligands. In addition to PVP, we separately functionalize the octahedra with thiol-terminated PEG-SH and 1-dodecanethiol via ligand exchange reactions. These surface capping agents are good representatives of hydrophilic and hydrophobic capping agents, and can form ordered self-assembled monolayers on the Ag surface. The functionalized octahedra are then assembled in the aforementioned solvents under identical conditions. Simulations of these ligands in various solvents are also conducted to observe the

changes in interaction between two clusters of the respective ligands. Their interaction energies in different solvents are also extracted.

The final goal is to map the “phase diagram” between the assembly product and the solvent-surfactant combination. Our first attempt was to prove that the choice of solvent can significantly affect the molecular interaction between PVP chains. The adsorption energy of PVP in different solvents is calculated. Two PVP chains with 125-repeat unit are placed in an $8\text{ nm} \times 8\text{ nm} \times 8\text{ nm}$ simulation box and the simulation is performed over duration of 60 ns.

During simulations, all trajectories are subjected to initial rough damping part just after the simulations are started. Also long fluctuation periods are found after equilibrium is reached. For the clarity purpose, these parts of the trajectories are not included. Also, due to the different damping and fluctuation time length, the figures in the sections are not showing the exact time scales. Each combination of surfactant and solvent is simulated for 2-3 times separately and the results are in little difference.

Figure 4.7 AA MD calculations of the interaction between PVP chains in different solvents. a, Plot of solvent-dependent PVP-PVP interaction energy. b, Equilibrium simulation snapshots of PVP chains in various solvents and SEM characterization shows the formation of well-aligned supercrystals in 1-hexanol, DMF, and water, whereas random aggregation is observed in toluene. All scale bars, 500 nm.

As shown in Figure 4.7 and Figure 4.8, Although attractive interaction always exist between the two PVP chains in all solvents at thermodynamic equilibrium, the interaction energy ranges from approximately -389 $k_B T$ in toluene to around -40 $k_B T$ in both 1-propanol and 1-hexanol. Simulation snapshots show the PVP chains associating with each other in these solvents (Figure 4.7b). Both interaction energy in Figure 4.7a and simulation snapshots in Figure 4.7b indicate that molecular interactions between two PVP chains depend significantly on solvent choice. Lower energy between PVP chains in 1-hexanol, DMF, and water environment will lead to a lower extent of overlap between the

polymer chains. Higher interaction energy between PVP chains in toluene leads to significant association between the two polymer chains. The much stronger interaction energy in toluene leads to greater overlap between the polymer chains, whereas weaker interaction energy in other solvents shows lesser extent of chain overlap. Simulation snapshot of the PVP chains in toluene also illustrate a much more rapid and irreversible chain association within a very short timeframe as compared to the PVP chains in water.

There is a strong relationship between molecular interactions on the nanoparticle surfaces and the success of Ag octahedra assembling into the Minkowski lattice. Weaker interaction energy, ranging from $-40 \text{ k}_B\text{T}$ to $-213 \text{ k}_B\text{T}$ in our simulations, is favorable for Minkowski lattice formation. This is observed in a range of relatively polar solvents, including 1-hexanol, 1-propanol, DMF, and water. PVP chains can be effectively solvated in these solvents to enable a stable dispersion of the octahedral nanoparticles in these solvents, allowing controlled organization of nanoparticles into ordered supercrystals. In contrast, strong interaction energy observed in a non-polar solvent such as toluene is correlated with a low solubility of the PVP chains, leading to rapid and irreversible aggregation.

Our results successfully establish the potential of using the molecular interaction energy between the surface capping agents (PVP) to predict the formation of Minkowski lattice in the experiments. Favorable solvent-dependent interaction between the PVP chains is a critical factor determining the successful formation of supercrystals, analogous to the importance of solvent choice in classical crystallization. At the same time, our findings signify the importance of molecular-level polymer-based interactions on nanoparticle surfaces in the self-assembly process, which are usually downplayed in alternative approaches such as hard polyhedra approximations.

After successfully correlate the interaction of PVP surfactant molecules to the thermodynamics prediction of assembly outcomes, which proven via experiments, we carried the simulation to other surfactant choices to finish the “phase diagram”. PEG-SH and dodecanethiol which are of quite different characteristic compared to PVP are introduced.

Figure 4.8 Interaction energy between PEG-SH chains in various solvents. The solvents are (a) water, (b), DMF, (c) 1-propanol, (d) 1-hexanol, and (e) toluene. All scale bars, 200 nm.

As shown in Figure 4.8, Minkowski supercrystal is observed for PEG-SH-functionalized Ag octahedra in relatively lower dielectric solvents (DMF, 1-propanol, and 1-hexanol),

where the interaction energies are comparatively weaker ($> -220 \text{ k}_\text{B}T$, Figure 4.8b-d). Simulation snapshots also show that the structural integrity of the two initial PEG-SH clusters is preserved at the end of the simulation, and PEG-SH clusters are favorably associated with each other. Thus, this leads to the formation of Minkowski supercrystal. On the other hand, the PEG-SH-functionalized octahedral nanoparticles aggregate randomly in water and toluene due to their strong interaction ($< -220 \text{ k}_\text{B}T$, Figure 4.8a). In water, PEG-SH readily interdigitates with other PEG-SH chains, and simulation snapshots show the two clusters merging into one (Figure 4.10c-iv, Figure 4.8). In toluene, PEG-SH chains cluster together rapidly, also leading to rapid particle aggregation.

Figure 4.9 Interaction energy between DDT chains in various solvents. The solvents are (a) water, (b), DMF, (c) 1-propanol, (d) 1-hexanol, and (e) toluene. All scale bars, 200 nm.

For 1-dodecanethiol covered octahedron nanoparticles, aggregation is always observed regardless of solvent choice. In lower dielectric solvents (1-propanol, 1-hexanol, toluene),

1-dodecanethiol molecules are stretched out, and simulation snapshots show that the molecules tend to interact more with the solvents than with each other (Figure 4.10c-ii, Figure 4.9). The interaction energies between 1-dodecanethiol are all stronger than -220 kBT in these solvents leading to uncontrolled aggregation of Ag octahedra in the assembly experiments Figure 4.10b-ii).

In higher dielectric solvents (water and DMF), the solubility of 1-dodecanethiol is comparatively lower, leading to a rapid association of the 1-dodecanethiol molecules due to the more favorable interactions among 1-dodecanethiol molecules (Figure 4.10c-iii, Figure 4.9). The interaction energies between 1-dodecanethiol reach around -1300 kBT in water, also leading to unfavorable conditions for the formation of the Minkowski lattice. Random aggregation of the octahedral nanoparticles is also observed when toluene is used as the solvent regardless of the ligand. The ligand interaction is strong, with interaction energies clustering around -400 kBT in toluene for all ligands.

Figure 4.10 the phase diagram which combines simulations with experiments to outline conditions favorable for the formation of Minkowski lattice. a, the axes of the phase diagram are constructed using the interaction energy between various surface capping agents in various solvents, while the dashed box shows regions where Minkowski lattice formation is observed from experimental observations; b, representative SEM characterization of the self-assembly outcomes for PEG-SH- (i, iv) and DDT-functionalized (ii, iii) Ag octahedra in the respective solvents. Scale bars, 200 nm; c, corresponding simulation snapshots of the molecular-level behaviors of PEG-SH (i, iv) and DDT (ii, iii).

To correlate the interaction energy values derived from the simulations with the self-assembly experimental observations, we construct a phase diagram to delineate conditions favorable for Minkowski supercrystal formation (Figure 4.10a). The interparticle interaction that greatly affected by surfactant and solvent combination is believed to have direct impact on the assembly. For example, too strong interaction would prohibit relocation after aggregation, leading to amorphous packing, while if the interaction is too weak, there would be little to hold the newly formed structure and collapse back to random state. This phase diagram charts the interaction energy changes with variations in solvent dielectric constants. Figure 4.10b and c show the SEM image and simulated polymer configuration at different points on the phase diagram. As mentioned earlier, PVP-functionalized octahedra crystallize into the Minkowski lattice in all solvents, except in toluene where the interaction between PVP chains is too strong. Also PVP and PEG-SH are more favorable in directing Minkowski assembly than 1-dodecanethiol. A general observation is that Minkowski structure formation requires the interaction energy between ligands to be weaker than approximately -220 kBT. The requirement for dielectric constants of the solvent has a board choice from just above zero to as high as 80 for water. Based on these findings, we could also make possible predictions on the assembled structure given the choice of surfactant and solvent combinations.

4.4 Outlook and Conclusion

Our results demonstrate the importance of surface functionality and how their molecular-level interactions directly impact the macroscopic crystallization of Ag octahedra into the Minkowski lattice. Attractive interactions between polymeric surface capping agents drive the particles towards each other to initiate the self-assembly process. We further establish an unprecedented phase diagram to combine both simulations and experimental observations into a standardized platform. This phase diagram uses interaction energy between several surface capping agents in various solvents to delineate favorable experimental conditions for close-packed structure formation. While this work focuses on the Minkowski lattice formed by octahedral particles, the importance of interactions between surface capping agents implies that our work can be readily extended to predict the self-assembly outcomes of other combination of surfactants and solvents thermodynamically.

Chapter 5

MD Simulation Study on Early Stage of PPHE Self-Assembly Processes

This chapter includes a study on kinetics and nucleation process of PPHEs. The hypotheses on governing interaction and control of assembly via environment modification proposed previously are considered valid and could further contribute in large particle amount kinetic simulations. Octahedron 3D close packing or Minkowski structure is translated into strict testing criteria for trajectory key frame analysis. Preliminary data on the initial nucleation stage of polymer covered silver octahedron PPHEs assembly is delivered. Justification and comparison with classical nucleation theory is also elaborated.

5.1 In-situ Investigation for Close Packing Nucleation of PPHEs

Aiming to approach this problem through another fundamental way, the reaction kinetic point of view, we utilize our previous results demonstrate the possibility of study the very initial stage of the assembly process. The study of nucleation and growth of octahedra particle would be a good start for similar study for PPHEs.

Classical nucleation process is well studied in exploring nucleation and growth behavior of a variety of matters, from water molecules to metallurgic crystallization, and it states:¹

$$R = N_s Z j e^{\frac{-\Delta G^*}{k_B T}} \quad 5-1$$

Where ΔG is the free energy cost of the nucleus at the top of the nucleation barrier, and $k_B T$ is the thermal energy with T the absolute temperature and k_B is the Boltzmann constant. N_s is the number of nucleation sites, and j is the rate at which molecules attach to the nucleus causing it to grow. Z is the Zeldovich factor Z , the probability that a nucleus at the top of the barrier can go on to form the new phase instead of dissolving.

This theory can match and explain well in nucleation associated with molecular level interactions such as water nucleate into ice.² Our interested PPHEs also form crystals when under close packing conditions. But under what condition and at what extend classical nucleation theory can apply still remains unclear. Plenty of examples have shown that the answers to crystal nucleation lay in the initial stage, and which are two modes to choose: homogeneous nucleation, or heterogeneous nucleation.^{3, 4}

For homogeneous nucleation, ΔG in Equation 5-1 follows:

$$\Delta G = \frac{4}{3} \pi r^3 \Delta g + 4 \pi r^2 \sigma \quad 5-2$$

Where Δg is the difference in free energy per unit volume between the thermodynamic phase nucleation is occurring in, and the phase that is nucleating. σ is the surface tension of the interface between the nucleus and its surroundings. r is radius of nucleus, assumed to be a sphere.

For heterogeneous nucleation, the controlling parameter is more on the interface surface energy. The ΔG is much smaller than that of homogeneous nucleation by several orders of magnitudes. And due to the geometry shape of heterogeneous surface, nucleation is usually much faster than homogeneous nucleation mode. The criterion for heterogeneous nucleation to happen is presenting an interface between nucleation particles and a different surface, with lower surface energy. In our simulation, our system is mimicking the bulk colloids of PPHEs, so we did not apply this different surface into the simulation, only focus on homogeneous nucleation.

On the other side, as the individual particle size of octahedra nanoparticle is enormous bigger than molecular level particles, the liability of classical nucleation theory may be questioned. After all, PPHEs are hardly sphere, which is an important assumption in classic nucleation theory. Also the timescale for nucleation and growth process could also vary from that of small and isotropic particles.

As a summary, for octahedra nanoparticle system our aim is to find out how fast the nucleation process happens and the principle of growth. We would investigate the initial stage of our MD simulations under different conditions on octahedron nanoparticles. If any classical nucleation rules apply, to how much extent does the classic nucleation theory holds would also be our focus of interest. After the study in octahedral system, further research to see if such classical principle can apply to other PPHEs system would be a great starting point for the future work.

5.2 Minkowski Structure Checking Criteria

To study the nucleation of octahedra shaped particles, firstly we should understand its packing mechanism to identify if the nucleation process is happening. As first discovered about a century ago, the Minkowski structure is consisting of primitive unit cell made up by 8 octahedra. Apart from its space fitting factor of 18/19, how these 8 octahedra contact each other still lacks straightforward expression. Since we are performing dynamic simulation on assembly of octahedron in three dimensional space, and need precise

guideline for telling whether a Minkowski structure is presented, it is inevitable to set up the checking criteria to analysis the trajectory frame.

For further breaking up of the structure, we assign the central octahedron that having contact with all other 7 octahedron as the base octahedron (Figure 5.1(a)). If the edge length of an octahedron particle is defined as a , and the diagonals of the central octahedron set as basis axis, then the unit cell parameters of Minkowski structure could be clearly defined in Table 5-1, Table 5-2, and Figure 5.1.

Figure 5.1 The schematics drawing of Minkowski configuration. a, a Minkowski unit consisting 8 octahedra. The red octahedron is the center reference as all other 7 octahedra are contacting it.; b,

three of them are type 1 contact showing in blue, with an overlapping surface of 4/9 of the triangle facet; c, three of them are type 2 contact showing in green, with an overlapping surface of 2/9 of the triangle facet; d, one of them are type 1 contact showing in yellow, with an overlapping surface of 6/9 of the triangle facet

To better investigate the inter-octahedron orientation relationship, the 7 non-central octahedra are separated into three categories of contacting patterns:

Type 1, configuration with tip of one octahedron touching 1/3 of the edge of the other octahedron, shown in Figure 5.1(b). The contact area is 4/9 of the triangle facet. It has two sub families. CoM distance is $\frac{a\sqrt{7}}{3}$.

Type 2, Configuration with tip of one octahedron touching the facet center of the other octahedron, shown in Figure 5.1(c). The contact area is 2/9 of the triangle facet. CoM distance is a.

Type 3, Configuration with the facet center of one octahedron touching the facet center of the other octahedron, shown in Figure 5.1(d). The contact area is 6/9 of the triangle facet. CoM distance is $\frac{a\sqrt{6}}{3}$.

For the sake of clear elaboration, we don't include partial octahedron in the unit cell. Every octahedron making up the unit cell is whole, and it is possible that some part of it can be outside of the cell. Under such framework, we developed the following criteria of Minkowski checking.

5.2.1 Diagonal relationship

Each octahedron has 3 diagonals. They are orthogonal to each other. For all octahedra in Minkowski structure, their diagonal systems are also in orthogonal relationship. In other words, each diagonal from one octahedron should have 0 degree angle with one diagonal

from the other octahedron, and 90 degree with the other two diagonals, as shown in Figure 5.2.

Figure 5.2 The spatial orientation relationship between two octahedra. The key references are the center of mass O (O') and its diagonals i, j, k (i' j' k').

5.2.2 Inter-octahedron distance

The distance between centers of mass (CoM) of two octahedra follows a fixed value for Minkowski structure. Depending on their contacting types, the values are: 0.882 edge length for 4/9 contact, 1 edge length for 2/9 contact, and 0.866 edge length for 6/9 contact. The schematic plot of each contacting types are showing previously in Figure 5.2.

Contact type	OO' vector	OO' distance
--------------	------------	--------------

Type 1a	$\left(\frac{\sqrt{2}a}{6}, \frac{a\sqrt{2}}{2}, \frac{a\sqrt{2}}{3}\right)$	$\frac{a\sqrt{7}}{3}$
Type 1b	$\left(-\frac{\sqrt{2}a}{2}, \frac{a\sqrt{2}}{3}, \frac{a\sqrt{2}}{6}\right)$	$\frac{a\sqrt{7}}{3}$
Type 1c	$\left(-\frac{a\sqrt{2}}{3}, \frac{a\sqrt{2}}{6}, -\frac{a\sqrt{2}}{2}\right)$	$\frac{a\sqrt{7}}{3}$
Type 2a	$\left(-\frac{\sqrt{2}a}{6}, \frac{\sqrt{2}a}{6}, \frac{a2\sqrt{2}}{3}\right)$	a
Type 2b	$\left(-\frac{\sqrt{2}a}{6}, \frac{a2\sqrt{2}}{3}, -\frac{a\sqrt{2}}{6}\right)$	a
Type 2c	$\left(-\frac{a2\sqrt{2}}{3}, -\frac{\sqrt{2}a}{6}, -\frac{a\sqrt{2}}{6}\right)$	a
Type 3	$\left(-\frac{a\sqrt{2}}{3}, -\frac{a\sqrt{2}}{3}, \frac{a\sqrt{2}}{3}\right)$	$\frac{a\sqrt{6}}{3}$

Table 5-1 Center of mass distance and vector between two octahedra of different Minkowski contact orientations.

5.2.3 Euler angle between octahedra

The last criteria for Minkowski contact is the angle between diagonal of the octahedron and the line connecting two CoMs. This angle can also be visualizing as the angel connecting vertex-CoM-CoM. For different contacting types, this angel is also different: it should be either 76.38 degree, 19.45 degree or their supplementary angels for 2/9 contact; either 74.46 degree, 57.72 degree or their supplementary angels for 4/9 contact; either 54.72 degree or its supplementary angle for 6/9 contact.

Contact	Possible angle between OO' and i, j, k
---------	--

type	
Type 1	76.38° 103.62° 19.45° 160.55°
Type 2	74.46° 105.54° 57.72° 122.28°
Type 3	54.72° 125.28°

Table 5-2 Euler angles between two octahedra of different Minkowski contact orientations.

5.3 Initial Nucleation Process Study on Silver Octahedron Assembly Process

In our silver octahedron systems, the close-packing cluster we are interested is Minkowski structure. After the rigid criteria for identifying Minkowski structures is secured, we analysed a number simulation trajectories to look for information on close-packing nucleation of PPHEs.

Trajectories are reprocessed by each time frame. Each octahedron in the system will be indexed. The coordinates of its 6 most central building spheres will be averaged for its central coordinate. The most 5 building spheres near each of its 6 tips will also be analysis for distortion check and averaged for the tips' coordinates. So we can have both the central coordination and its axis information for further analysis. The maximum deviation range for the numerical data is set as 1%.

5.3.1 Nucleation Process on Silver Octahedron Assembly

The models used in this session are coarse grain octahedron containing silver core and polymeric surfactants, inheriting the design of model discussed in chapter 3. Each octahedron contains 670 building spheres. To investigate the nucleation process on PPHE particle, we performed NVT and NPT simulations to represent the natural nucleation happening in dilute and concentrated bulk colloid systems.

Firstly, we tested the 63 octahedra particles system with random initial configurations for 400 ps. The time step for this simulation is 0.002ps and after each 500 steps a frame containing coordination will be recorded. The geometry of the model is a miniaturized version of the experimentally synthesized Ag octahedra with 1/100 of the original edge length. Shrinking the model size speeds up the time scale of the self-assembly process during the simulations, and enables us to observe the initial stage of the self-assembly process within a reasonable timeframe. 63 of such octahedra are randomly oriented inside a $17 \times 17 \times 17 \text{ nm}^3$ simulation box, corresponding to a relatively low initial volume filling fraction of 16.7% (Figure 5.3a). Simulations are run under isothermal-isochoric conditions at 273K, with the size of the simulation box size is fixed during the process.

Figure 5.3 NVT dynamic simulation on 63 randomly ordered octahedron nanoparticles, with blue particles indicating non-contact or non-Minkowski aggregation. a, random initial configuration; b, simulation result after 400ps; c, sample of Minkowski cluster in b; d, time evolution on Minkowski cluster and number percentage.

Such CG model MD simulation is intended to explore the very initial stage of the self-assembly process. From its data we could have qualitative understanding of nucleation and later growth, thus allowing us to know where to focus if we want to have the nucleation process better studied.

Significant assembly of the octahedra into the Minkowski cluster is observed during the simulation. The octahedra highlighted in red in Figure 5.3b corresponds to those clustered into Minkowski lattice, 25% of the octahedra are observed to form the Minkowski lattice.

The largest cluster observed corresponding to a hexamer (Figure 5.3c). Once formed, the clusters didn't show de-assembling behavior within the simulation time (Figure 5.3d). Moreover, from the result shown in Figure 5.3d, we also know where to look deeper in the initial nucleation process. The first 10ps includes a great shoot-up for nucleated clusters for this NVT run. We further performed the simulation with all the same setup except the coordinates will be stored every 50 steps, which corresponds of 0.1ps.

At the same time, we also perform an NPT simulation fixed at 1 atmosphere pressure on the first 50ps, to find out how nucleation will proceed if the bulk colloidal system is concentrated. Instead of getting more diluted after aggregation in NVT case, particles will replenish themselves in system that is drying. The setup is the exact same initial configuration except the box size is allowed to be changed during the process and the coordinates will be stored every 250 steps, which corresponds of 0.5ps.

Figure 5.4 Time evolution on Minkowski cluster and number percentage for NVT (a) and NPT (b) simulation on 63 octahedra with random initial configuration.

The closed-up simulation about the initial nucleation of diluted colloidal system and concentrated bulk system finished with the results shown in Figure 5.4. As shown in Figure 5.4a, there is a gradual increase of the number of Minkowski clusters. Joined with several temporary plateaus each lasts for several picoseconds, such increase in nucleated

sites reaches its peak at 9 around 8 picoseconds. The switching between plateau and increment is possibly the overall outcome of nucleation and dissolving.

After the peak, the system might overshoot its nucleation process. With a little decrease in nucleated site number, the system researches its stable site number in equilibrium. At this stage, the site number is between 5 and 6 (Figure 5.4a). Then the system continues to grow these sites. By comparing Figure 5.3d and Figure 5.4a, it is observed that in long term aggregation and growth process, the stable number of sites for dilute colloidal system is around 4 to 5, slightly less than just after nucleation. It is possible that nucleated cores can fuse into one during the process. Also, as the time progress, there is a constant Minkowski orientated octahedra rate at around 20 to 25% as a proof of stable outcome of Minkowski assembly that does not dissolve back in to the suspension system.

Then, we move from random initial position to order initial position cases. The concentration is still at relative low level around 20%. The system is consisting of 64 octahedra forming $4 \times 4 \times 4$ array, in a simulation box of $16 \times 16 \times 16 \text{ nm}^3$. There are total 4 sets of initial configurations: One with zero rotation of the octahedra; other three sets consist octahedra with random initial rotation. The NVT simulation of 10 ns shows similar outcome for all initial configuration. The aggregation clusters observed for the 4 runs are 3, 2, 2 and 4 respectively.

For diluted system, these results show a possible growth limitation for fixed low concentration system. However, from Figure 5.4b, we can see some different trend for self-dense system, possibly systems that are getting dried. The increment in Minkowski nucleated cores and Minkowski oriented octahedra number are both greater than the diluted case. Such violent evolution takes also longer to reach its equilibrium state. It takes 20 to 30 picoseconds for both number of Minkowski sites and Minkowski oriented octahedra rate come to a relative stable stage. The fluctuation for later part of the simulation is also bigger than NVT case. It could be possibly understood by greater fusion and reorganization between cores due to strong contraction and densification of the system. As the result, the nucleated sites are stable around 7 to 10, and total Minkowski oriented particle rate is stable around 35% to 40%.

For nucleation process, the system status could lead to quite different outcomes. The diluted colloid system without contraction could only be able to produce less cores and closely packed clusters. When the system is under densification due to possible drying process, more violent process would be happening and more cores and closely packed particles would be found. We would discuss more of how system conditions affect the later stage of aggregation in the next session.

Figure 5.5 Aggregation simulation initial state and results between small clusters, with their time evolution graph. a, two tetramers; b, four dimers; c, two Minkowski unit cells.

Besides the nucleation process of monomer octahedron particles, the readily pre-formed octahedra dimers, tetramers and octamers (or Minkowski unit) can also be nucleated into

larger Minkowski clusters within a short time (Figure 5.5). We wonder how the initial seed would affect the nucleation process. Figure 5.5a is the case for two tetramers getting contact to each other. They form a Minkowski unit after 10ps, which is not obviously slow compare to monomer case. It could be highly possible that the two tetramers are facing each other with a large surface, increasing the interaction between them that results a fast aggregation. If we reduce the exposing surface by making it 4 dimers (Figure 5.5b) or increasing the mass of each cluster (Figure 5.5c), the aggregation time significantly increases. Eventually they will form a single cluster, but the larger they are, the more the nucleation process would be hindered. Another interesting finding is that the surface area would still play its roll in PPHE assembly although the size is in hundreds of nanometers.

From these investigations, the results are showing that the process of the nucleation process begins in continuous medium from a random initial state, leading to the formation of dimers and small clusters, even under relatively low volume filling fractions, which was previously considered to be not likely to happen. The initial nucleation process for silver octahedron systems is very fast and within several ps. Once formed, the interaction between the particles would hold most of them from dissolving back. However, larger clusters would require much more time for aggregation to happen.

5.3.2 Effect of Particle Density on Cluster Size Growth

Besides the very initial stage, we further look into the later part of self-assembly process of PPHEs. Many factors would have their influence on growth process and the first of many questions is how the density of nanoparticles will affect the growth process since it is a very realistic problem that faced in experiments, later stage of the dried colloid system.

To achieve this goal, an initial state with relatively more order and higher volume density is also adopted. The initial volume filling fraction of the simulation box is further increased to 35.7% (Figure 5.6a) compare to 16.7% in random case (Figure 5.3a) by

placing 72 spatial denser packed octahedra into a $12 \times 12 \times 16 \text{ nm}^3$ simulation box. It is denser but absolutely non-Minkowski-structured. Their diagonals are not orthogonal, and their Euler angles and interparticle distance are also far from Minkowski criteria. This setup is to better approximate the experimental self-assembly conditions of high particle densities, especially when lots of the solvent is losing during drying. The simulation box also undergoes a volume reduction under isothermal-isobaric conditions during simulation. The time step is still 0.002ps but since we are more interested in the overall growth process, the simulation time is 400ns with frame rate of 5000 steps.

Figure 5.6 NPT dynamic simulation on 72 semi-ordered octahedron nanoparticles, with blue particles indicating non-contact or non-Minkowski aggregation. a, random initial configuration;

b, simulation result after 400 ps; c, sample Minkowski cluster in b, which is much larger than Figure 5.3c; d, time evolution on Minkowski cluster and number percentage of NPT run.

From the results, we can see that quite a number of the octahedra are assembled into the Minkowski lattice showing in red after 400 ps (Figure 5.6b). The largest Minkowski cluster comprising 25 octahedra (Figure 5.6c). The total Minkowski structure rate reaches as high as 60% in the first tens of ps, and holds at such level to the end of the simulation (Figure 5.6d). The final volume filling ratio is 94.4%, closely matching the packing density of the Minkowski lattice at 94.7%, indication very similar packing of real Minkowski structure. The number for Minkowski clusters is varying greater than the less dense case (Figure 5.3d), due to high particle density could possible introduce the particle diffusion at the surface. With the newly formed cluster may not closely interlocked, such sliding back and forward movement may be the cause of the fluctuation in Figure 5.6c.

The simulations at both low and high volume filling ratios both suggest that the formation of Minkowski structure could spontaneously happens in suspended condition. However, in case of sedimentation and evaporation process, the polymer layer will shrink and greatly reduce its interaction. So after we answer the question about how the density affects growth, we further work on systems with readily formed close packing.

Figure 5.7 NPT dynamic simulations on semi-ordered initial configuration of different system sized. a, initial near-Minkowski initial configuration of 8 octahedra; b, NPT simulations results of 8 octahedra; c, initial near-Minkowski initial configuration of 72 octahedra; d, NPT simulations results of 72 octahedra; e, initial near-Minkowski initial configuration of 216 octahedra; f, NPT simulations results of 216 octahedra

Our next question is that after the solution is almost dried out, when the polymer shell outside PPHE would possible lose its function, will the readily formed near closed packing structure still hold or fall into pieces? As previously demonstrated, the 3D self-assembly begins in continuous phase. Octahedron particles first get close to each other by PVP interaction and then become denser by evaporation. What will happen after the PVP shell shrinks? Would it follow the further attraction between Ag cores to get even denser?

To demonstrate such shrinking process after self-assembly of bulk Minkowski structure, an initial state with Minkowski lattice (8, 72, and 216 particles) is constructed firstly. Then the near-Minkowski structure is built by deleting the PVP outer layer (Figure 5.7a, c, and e). 200ps of simulation is performed on 8 octahedra case, and 400ps is ran for 72 octahedra case, and 750ps for 216 octahedron case. All simulations are in NPT setup with 0.002ps time step. From the results, still quite a number of the octahedra are still assembled into the Minkowski lattice after the equilibrium state is reached. For 8 octahedra case, 6 of them still hold in Minkowski structure and the two loose particles are also attached with the rest (Figure 5.7b). Although not perfectly contact in Minkowski way, the difference is very small. It is hard to tell from a real Minkowski unit cell. For larger cases of 72 and 218 octahedra cases, still more than 50% of the particles are in Minkowski structure. It is to be noted that due to the long simulation time and very high initial density, there are several octahedra suffer from sliding of its own building spheres, making our checking criteria failed for 11 and 23 octahedra for these two cases, although from observation, many more of the particles arrange like Minkowski structure. We believed that the true outcome would be much higher than 50% in Minkowski structure rate.

The result testifies such assumption that the energy difference would prefer towards the low-energy Minkowski lattice structure: initially because of in continues solution system with good PVP solubility in terms of surface energy, it is easy to assembly into low energy lattice and have enough time to relax; then the self-assembly proceed in solution phase, getting particles close to each other via PVP interaction; finally by evaporation and sedimentation, the structure would become denser after PVP layer is dried out.

During the studies on initial assembly process of octahedra nanoparticles, we aware that there are two major biases in the studies using CG model. The first one is that the simplification of octahedron particles. Whether the outer shell can perform properly as the all-atomic polymer surfactant molecules would be a concern. The parameter for the outer layer is adopted from previous calculations in section 4.2.2, and it is believed to project the most of PVP surface at the maximum simplification in calculation. The second is initial configuration related bias. It would be problematic in general simulations, though the main goal here is to find out the controlling factor from the initial density. The additional artificial would be an advantage in accelerating the assembly process. The simulations in the above section show a preliminary correlation between particle density and the initial cluster size and distribution. Nevertheless, full qualitative understanding of the effect from these biases would be one of our next goals.

5.4 Outlook and Conclusion

Our results could serve as an initial attempt to demonstrate the usefulness of simulation treating the PPHEs assembly system. The initial assembly process for PPHE is studied via MD simulations with in-situ analysis methods. This work suggests a new possible path to unveil the complicated mechanism of PPHEs self-assembly.

We approached the nucleation and growth study for octahedron firstly through its mathematical expression on the geometry of orientation and interpositions. With checking criteria ready, we performed and analysed a number simulation to look for the information on nucleation and growth.

The initial nucleation process for octahedron PPHE systems is within several picoseconds. For nucleation process, the diluted colloid system would produce less cores and closely packed clusters compared to systems under drying process. For NPT simulation representing such densification procedure, more cores and closely packed particles had been found.

Also we studied other properties and factors that could affect the aggregation. For cluster size, larger clusters would require much more time for aggregation. And even after the outer shell loses its interaction due to dehydration after the drying process, the condensing effect and interaction between metal cores of the octahedra would still hold the Minkowski structure not falling apart.

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Chapter 6

Summary and Recommendations for Future Work

This chapter includes two sections, a summary of the whole thesis and a brief introduction and suggestion on the future works. The works presented in this thesis have solved some of the problems that stand in the path of PPHE self-assembly studies. The preliminary works have shown that to what extent interparticle interaction could affect the outcome of the assembly. Together with other controlling parameters, it is even possible to quantitatively predict the behavior of PPHE assembly in the form of phase diagram. On the other side, MD simulations prove again its usefulness in octahedra PPHE nucleation and growth analysis. This could be easily adapted to other PPHE system, as to open the whole new aspect of PPHE assembly research.

6.1 Summary

In this thesis, Chapter 1 states the current problems, significance, our hypothesis, and research scope. It also provides a brief introduction of the overview structure of later chapters.

In chapter 2, a brief review of the current state of simulation technique and research related to nanoparticles system is presented. Process of nucleation mechanism studies in nanoparticles is also reviewed in this chapter, together with several reports on experimentally observed PPHE assemblies.

In the chapter 3, it illustrates how simulation models are constructed based on the fact that nano-octahedron particle possessing the size and atom number far beyond the treatable limit of all-atom molecular dynamics. Then we introduce strategies of using separated modeling methods to deal with this problem. Interaction energy for general surface case and specific stacking patterns are also described.

In chapter 4, thoughtful study of investigating interparticle interaction was performed. The first hypothesis regarding the surface interaction dominance was validated via the investigation of interparticle interaction from each component of the particle. The second hypothesis of controlling assembly of PPHEs was also proven by successfully relating the thermodynamic outcome of assembly with qualitative physical quantity of surfactant hydrophobicity and solvent polarity.

In chapter 5, we explored the nucleation and growth process of octahedron PPHEs. Together with well-established octahedron aggregation pattern characterization criteria, in-situ analysis for Minkowski structure has been possible. In-situ simulation instigation was done for the nucleation process and many more MD runs are conducted to study the controlling factor of Minkowski structure growth during and after the process of drying of the colloidal PPHE system.

This whole work on octahedron nanoparticles self-assembly uncovered the very small corner of the PPHE aggregation field. We are confident that much more could be achieved by future researches. From our heart, we wish a new breakthrough in

connecting the microscopic world in nanometer level and the macroscopic world that we live in is not far away.

6.2 Recommendation for Future Works

There are several possible directions of future works. Among them, further studying the PPHE assembly mechanism by applying the simulation to different PPHE systems is the most straight forward one. Different PPHEs are more than just different in the shape, but also differ in other aspects that requiring efforts in future works.

Figure 6.1 Other common PPHE samples, namely tetrahedron, cube and truncated cube.

As shown in

Figure 6.1, some the other typical PPHE samples may have much difference in their geometry. To study their assembly mechanism, several works must be done.

Firstly, the close packing of the corresponding geometry must be identified. This is to ensure rigid mathematical checking criteria for in-situ trajectory analysis could be possible.

Secondly, valid modeling protocols need to be established. For octahedron, we adopted hard spheres as building blocks. Similar procedure could also be introduced to other geometries, with possible alterations. For instance, spheres may not go quite well with the cubic structure. The orthorhombic corner is not the natural closely packing structure for spheres (

Figure 6.2). How to co-op with this problem is one of the main challenges for modeling PPHEs in small building blocks.

Figure 6.2 Orthorhombic stacking of 8 spheres. The structure is neither closely packed nor stable.

Thirdly, interparticle interaction profile could be of great difference between different PPHEs. For octahedron, the case is already complicate enough that we have to separate a pair of octahedra for detailed study. For very sharply shaped geometry such as tetrahedron, the small number on facets means a vast influence from interparticle orientation in interaction. On the other hand, for more spherically shaped geometries like the truncated cube, this effect delays quite a lot. Thus, more detailed profiling for different PPHE system is always needed. This posts another major work direction for the future works.

Fourthly, simulation is a power tool in exploring PPHE self-assembly mechanism. It does can obtain information that experiments cannot collect. However, for any research to be firm and well-proved, experimental observation and proof are not to be ignored. The best thermodynamic evidence, the final assembly outcome can be obtained in laboratory. The experimental technique has developed mutual protocols for synthesise nanoparticles with

many geometry choices. Thus suggesting and possibly designing for any upcoming experiments would be on the list of future works.

We have come to this far in connecting the nanoparticle study to the macroscopic self-assembly process. With more effect in the future, the secret of PPHE self-assembly mechanism that can greatly benefit mankind in manufacturing, medication, function material production and nanomachine would be finally unveiled.